STi
Sonoma Technology, Inc.

EMISSION INVENTORY RECONCILIATION IN THE CRPAQS STUDY AREA

California Regional PM$_{10}$/PM$_{2.5}$ Air Quality Study (CRPAQS)
Data Analysis Task 4.2

FINAL REPORT
STI-902327-2751-FR

By:
Sean M. Raffuse
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Sonoma Technology, Inc.
Petaluma, CA

Prepared for:
California Air Resources Board
Sacramento, CA 95814

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1. INTRODUCTION

Emission inventories are the foundations of air quality modeling and regulatory control strategy development. Because of the complexities involved in developing emission inventories and the effect of errors in the inventory on air quality model performance and control strategy assessment, it is important to evaluate the accuracy and representativeness of any inventory that is intended for use in air quality modeling. Several techniques are used to evaluate emissions data: "common sense" review of the data; bottom-up evaluations that start with emissions activity data to estimate corresponding emissions; and top-down evaluations that compare emission estimates to ambient air quality data or that use ambient data to estimate emissions profiles. This work represents a top-down emission inventory evaluation approach using surface ambient data.

Sonoma Technology, Inc. (STI) conducted a top-down inventory evaluation to identify areas of the emission inventory that potentially need improvement. The approach used for this study is a technique termed "emissions reconciliation". An emissions reconciliation is a selective, quantitative comparison of emission inventory- and ambient-derived pollutant ratios (e.g., volatile organic compounds [VOC]/oxides of nitrogen [NO_x], particulate matter [PM]/NO_x). Findings often point toward weaknesses or omissions in the emission inventory, which can be iteratively remedied until the inventory and ambient data reconcile with one another (Haste et al., 1998; Korc et al., 1995; Fujita et al., 1992). The findings of an emissions reconciliation study can be used to improve an emission inventory prior to air quality modeling.

1.1 BACKGROUND AND OBJECTIVES

The objective of this work is to evaluate the hourly emissions inventory for different regions within the San Joaquin Valley (SJV) using 2000 and 2001 ambient data collected during the California Regional PM_{10}/$PM_{2.5}$ Air Quality Study (CRPAQS). Similar work completed during the Integrated Monitoring Study 1995 (IMS-95) indicated several areas of the emission inventory that could be improved. This work focused on assessing how well more recent emissions estimates represent real-world pollutant concentrations in the SJV. Where possible, we directed particular attention to understanding how ambient pollutant concentration ratios vary by day of week and if these variations are captured in the emission inventory.

Comparisons of ambient- and emission inventory-derived primary pollutant ratios have proven a useful tool for improving emissions estimates. However, these types of comparisons are confounded by the fact that ambient concentrations are influenced not only by fresh pollutants, emitted in the near vicinity of a monitor, but also by aged pollutants transported from sources farther away and the chemical reactions that may have occurred after the pollutants were emitted. The influence of these effects on the comparisons can be minimized (but not eliminated) by selecting ambient data collected at times when emission rates are high and chemical reaction rates are low. Morning sampling periods offer the best potential to minimize the effects of the latter influences in the ambient/emission inventory comparisons. Emissions are generally high during morning hours, mixing depths are low, and long-range transport and chemical reactions are minimized. It should be recognized, however, that NO_x emissions from

elevated sources may be injected above the morning inversion and, hence, may not affect surface-level concentrations. Evaluations with and without elevated NO_x sources were performed to understand their potential influence on the ratio analyses.[1]

1.2   OVERVIEW OF TECHNICAL APPROACH

Using ambient measurements collected during the CRPAQS field study, STI spatially compared emissions estimates with ambient air quality data by calculating emission inventory- and ambient-derived primary pollutant ratios of VOC/NO_x, carbon monoxide $(CO)/NO_x$, sulfur dioxide $(SO_2)/NO_x$, and $PM_{2.5}/NO_x$. Primary pollutant ratios were compared for four urban sites and one rural site.[2]

The scope of work for the emission inventory evaluation task was divided into two work elements:[3]

1. Site selection and data processing

2. Comparison of emission inventory and ambient primary pollutant ratios

The technical approach for each of these work elements is described below.

1.2.1   Site Selection and Data Processing

STI consulted with California Air Resources Board (ARB) to select five ambient monitoring site locations for which to compute pollutant ratios for comparison with the emission inventory. Criteria for site selection included (1) a mix of urban and rural sites, (2) a mix of sites in and around the SJV, and (3) sufficient data from each site to conduct an analysis. The sites selected were Fresno First Street, Bakersfield, San Jose, Sacramento Del Paso Manor, and Bethel Island.

Of great importance to this effort is the ability to accurately match emissions information with ambient air quality data. The most appropriate comparisons for this type of evaluation should be based on individual chemical species, or compound groups, to the extent possible. ARB supplied STI with the latest available gridded, hourly, criteria pollutant and speciated VOC emission inventories. The speciated PM inventory developed for PM modeling was provided by the University of California at Davis (UCD). This inventory includes 18 components and 8 size bins.

STI processed the ambient air quality and meteorological data, collected at (or near, for meteorological data) the five sites, into formats needed for comparisons with the emission inventory. Statistical analyses performed on the ambient air quality data include calculations of minima, maxima, averages, medians, and confidence intervals. STI analyzed validated surface

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[1] Elevated point sources release emissions at a height above the first layer of the 3-dimensional air quality modeling grid (typically, above 25 to 50 meters).
[2] Ratios calculated for each site varied depending on the data that were available and valid for the analysis period.
[3] A third task to evaluate primary versus secondary organic and inorganic aerosols was completed as part of CRPAQS Task 6.2.

meteorological data to understand and account for the potential influence of meteorology—in particular, wind speed and direction—on the ratio comparisons.

A significant fraction of $PM_{2.5}$ mass is attributed to secondary aerosol formation in the atmosphere. Unfortunately, the emission inventory only accounts for primary aerosols. To compare the $PM_{2.5}/NO_x$ ratios from the emission inventory and ambient data, we used speciated $PM_{2.5}$ measurements to estimate the portion of aerosol mass that was associated with primary emissions.

1.2.2 Comparison of Emission Inventory and Ambient Primary Pollution Ratios

VOC/NO_x, $PM_{2.5}/NO_x$, CO/NO_x, and SO_2/NO_x ratios were computed for the selected sites from both ambient and emission inventory data. Each site provided a different suite of pollutant data sets for analysis. For all pollutants with hourly ambient data available (CO, SO_2, NO_x), ambient-derived ratios were compared with emission inventory-derived ratios by spatially matching ambient data by wind quadrant and speed to corresponding grid quadrants (groups of grid cells) surrounding the ambient monitoring site. At low wind speeds, only nearby grid cells were included in the analyses. A grid cell was included if an air parcel from the cell could theoretically reach the site within an hour at the observed wind speed. We used all grid cells within 20 km of the monitoring site to calculate emission inventory ratios for $PM_{2.5}$ and VOCs because of uncertainty in wind speed and direction over the five-hour sampling period for VOCs.

The speciated VOC emission inventory provided by ARB contains hundreds of chemical species. To perform a meaningful comparison between the emission inventory and ambient data, only those species detected by the ambient instrumentation were used in the comparisons.

1.3 UNCERTAINTY ISSUES

Understanding the uncertainties associated with comparisons of ambient- and emission inventory-derived pollutant ratios is essential to assess the suitability of top-down evaluation analyses. Three general categories of uncertainty issues are associated with top-down emissions reconciliation analyses: (1) accuracy of the emission inventory, (2) accuracy of the ambient concentration measurements, and (3) suitability of comparisons.

1.3.1 Emission Inventory Uncertainties

To compare ambient pollutant ratios to emission inventory ratios, it is important to accurately characterize, to the extent possible, the magnitude, spatial distribution, chemical composition, and diurnal pattern of emissions. Uncertainties and inaccuracies associated with emission inventory data generally result from (1) emissions estimation techniques and (2) emissions processing techniques. Inaccuracies and uncertainties associated with emissions estimation techniques include misclassification or exclusion of major emissions sources, the use of incorrect emissions activity data, the use of incorrect emission factors, and the use of incorrect chemical speciation profiles.

To perform an emission inventory evaluation, emissions estimates must be spatially and temporally resolved for the region surrounding the ambient monitoring sites. To accomplish this, hourly, gridded, speciated emissions estimates of VOC, NO_x, CO, SO_2, and $PM_{2.5}$ were acquired from ARB and UCD. The methods used to disaggregate annual average countywide total emissions estimates into gridded, hourly data can introduce inaccuracies in the emission inventory data. Spatial surrogate data that are not representative of the locations of emissions sources, and temporal profiles that are not representative of the monthly, weekly, and diurnal distribution of emissions source activity, can result in misrepresentation of the geographic location of emissions sources and diurnal activity patterns for sources within the vicinity (grid cells) of the ambient monitor.

Chemical speciation profiles are used to estimate the chemical composition of the emission inventory. Incorrect assignments of speciation profiles to emissions sources and/or speciation profiles that do not represent the chemical source composition can create emission inventory uncertainties.

1.3.2   Ambient Measurement Uncertainties

Uncertainties associated with ambient measurements include the influence of instrument detection limits, precision of measurements, and sampling and handling losses. Prior to conducting an emission inventory evaluation, the ambient data measurement methods should be assessed to ensure that the collection methods yield adequate data for this type of analysis. Furthermore, the ambient data sets intended for use must be quality-assured to eliminate invalid samples. For this study, ambient data were validated as part of CRPAQS Task 6.2.

1.3.3   Uncertainties Associated with the Comparisons

Uncertainties associated with the comparison of ambient and emission inventory data arise from the spatial and temporal matching of ambient and emission inventory data, meteorological factors, and atmospheric reactions. To minimize differences between ambient and emission inventory ratios resulting from mismatch in time and space, using emissions estimates as close to the vintage of the ambient data as practical yields the best outcome. For this study, emissions estimates representative of winter 2000 were compared to ambient data for winter 2000/2001.

Two key assumptions are employed when performing a top-down comparison of ambient- and emission inventory-derived pollutant ratios: (1) a major premise of the top-down evaluation is that only monitoring sites and sampling periods dominated by fresh emissions be considered in the analysis; and (2) estimates of NO_x emissions are relatively accurate (compared to estimates prepared for other pollutants) because they are emitted predominantly from combustion sources, for which activity data and emission factors are reasonably complete and representative. It is possible that temporal uncertainties may be caused by early morning ambient ratios that include carryover emissions in which VOC and/or NO_x have been preferentially removed by chemical conversion overnight. Spatial uncertainties may arise due to different influences of surface and aloft emissions. For example, VOC, PM, and NO_x emissions

from nearby elevated sources may be injected aloft and, as a result, may not mix into the surface air sample containing VOC, PM, and NO_x emissions.

Meteorological factors such as wind speed, direction, and mixing depth determine the spatial distribution of emissions and, thus, which emissions are sampled. For example, emissions from non-homogenous area and/or motor vehicle sources might be incompletely sampled at a given site. Atmospheric reactions modify the species distributions and mass of midday and afternoon ambient samples. Thus, comparisons during midday and afternoon periods are likely to be less reliable than morning comparisons.

Secondary aerosol formation in the atmosphere contributes to the mass of measured ambient $PM_{2.5}$. Because the emission inventory accounts only for primary PM emissions, the primary fraction of ambient $PM_{2.5}$ mass must be estimated to perform the ratio comparison. This estimation adds uncertainty to the $PM_{2.5}/NO_x$ ratio analysis.

1.4   RESULTS

Table 1-1 summarizes the overall results for each pollutant. The results of the ratio analyses are detailed by pollutant in Section 3.2.

Table 1-1. Summary assessment of pollutants in the CRPAQS emission inventory.

Pollutant	Status in Inventory	Comparison of the Ambient and Inventory-Derived Ratios
SO_2	Good	Comparison is within 20% in the late morning hours (0800-0900 PST).[1]
CO	Underestimated	Difference is greater than 50%.
VOC	Slightly underestimated	Difference is within 50%.
$PM_{2.5}$	Overestimated	Difference is greater than 50%.
NO_x	Early morning (0500-0700 PST) emissions from area sources are underestimated; but emissions are good otherwise.	Difference is greater than 50% or within 20% (depending on the site and time period).

[1] Underestimated NO_x emissions affect the comparisons during the early morning hours (0500-0700 PST).

2. DATA ACQUISITION AND PROCESSING

Preparing ambient concentration, meteorological, and emission inventory data for use in a top-down emissions reconciliation analysis involves several steps. This section presents a detailed discussion of the data preparation and processing performed for this emissions reconciliation.

2.1 AMBIENT MONITORING SITES AND DATA AVAILABILITY

Data used in this analysis were collected during the winter intensive monitoring period of the CRPAQS field study, December 18, 2000–January 24, 2001. The ambient data used for the ratio analyses were limited to data collected during morning (0500 through 1000 PST) because morning sampling periods offer the best potential to minimize the effects of chemical reaction rates on the ambient- and emission inventory-derived ratio comparisons. Emissions rates during the morning period are generally high, mixing depths are low, and long-range transport and chemical reactions are minimized. In addition, ambient data were segregated by weekday and weekend days where possible. Studies have shown that emissions activity patterns and ambient pollutant concentrations can be significantly different on weekdays relative to weekends (Fujita et al., 2003; Chinkin et al., 2002).

2.1.1 Ambient Site Characterization

To help identify and characterize land-use patterns and emissions sources surrounding each ambient monitoring site, readily available digital images were obtained. These images are based on United States Geological Survey (USGS) Digital Orthophoto Quarter Quadrangles (DOQQs), and vary in date of photography. The white dashed lines imposed on **Figures 2-1 to 2-5** indicate the approximate configuration of wind quadrants surrounding each site. Land use characteristics and emission sources are discussed in detail below.

Bethel Island

The Bethel Island Road monitor is located in the delta of the San Joaquin River, about 2.5 km south of the small town of Bethel Island (population < 2,500). As part of the field study component of the CRPAQS project, STI personnel recorded land use and individual point sources in the 1 km^2 area surrounding the site. The area around the site is shown in Figure 2-1.

Wind Quadrant 1 (1°–90°, Northeast) – The area immediately surrounding the Bethel Island monitoring site is farm and range land in all quadrants. Single family homes or camp sites line the banks of the sloughs of the San Joaquin River to the north in Quadrants 1 and 4, less than 1 km north of the site. The town center of Bethel Island is in this quadrant. Quadrant 1 is dominated by a large state water recreation area.

Wind Quadrant 2 (91°–180°, Southeast) – Quadrant 2 consists entirely of agricultural fields and water.

Wind Quadrant 3 (181°–270°, Southwest) – Quadrant 3 southwest of the railroad tracks is occupied by part of Oakley, a town with a population of about 25,600 (2000 Census). North of the tracks is another small town, Knightsen.

Wind Quadrant 4 (271°–360°, Northwest) – The remaining land in Quadrant 4 is rural residential, farmland, and water.
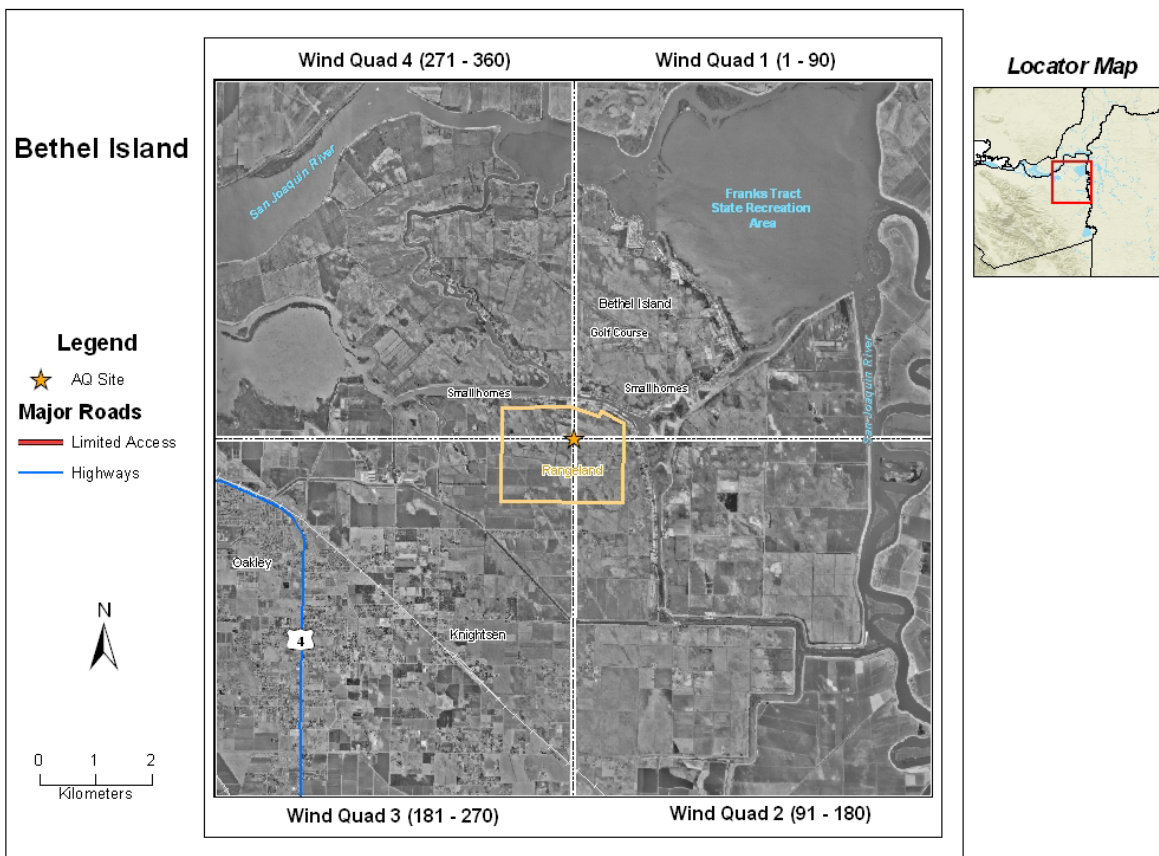
Figure 2-1. Map of the 10-km by 10-km area surrounding the Bethel Island ambient monitoring site.

Bakersfield California Avenue

Figure 2-2 shows the area surrounding the Bakersfield California Avenue monitor, located south of the Kern River, between residential and commercial areas (shopping, business parks, hospitals, restaurants, and hotels).

Wind Quadrant 1 (1°–90°, Northeast) – Quadrant 1 east of the site and south of the Kern River is commercial, giving way to residential area within about 1 km east of the monitoring site. North of the Kern River is a commercial/industrial area, served by a spur from one of the railroads that form a triangle in this quadrant. Some commercial/industrial development follows the railroad. South of the river, and north of the river outside the railroad triangle, are largely residential/commercial areas.

Wind Quadrant 2 (91°–180°, Southeast) – Immediately southeast of the monitoring site is a mixed residential/commercial area. This type of land use dominates the entire quadrant and includes a large shopping center and several parks and recreation centers. Toward the east boundary of the quadrant are the municipal airport and county fairgrounds.

Wind Quadrant 3 (181°–270°, Southwest) – The eastern part of Quadrant 3 is largely residential/small commercial. A large country club is situated less than 1 km directly southwest of the monitoring site; numerous small parks and two more large country clubs lie farther southwest from the site. The campus of the California State University at Bakersfield is about 3 km west of the site. The far western and part of the southern boundaries of the quadrant are occupied by field crops.

Wind Quadrant 4 (271°–360°, Northwest) – The area from the monitoring site to the northwest, about 1 km to the Kern River, is a mixture of residences and businesses. Across the river is an oil refinery, about 2 km northwest of the site. Just north of the oil refinery, about 2.5 km from the site, is a commercial recycling plant where concrete and asphalt are crushed and recycled for its parent paving company. The remainder of Quadrant 4 consists of small towns, rural residential areas, and agriculture.
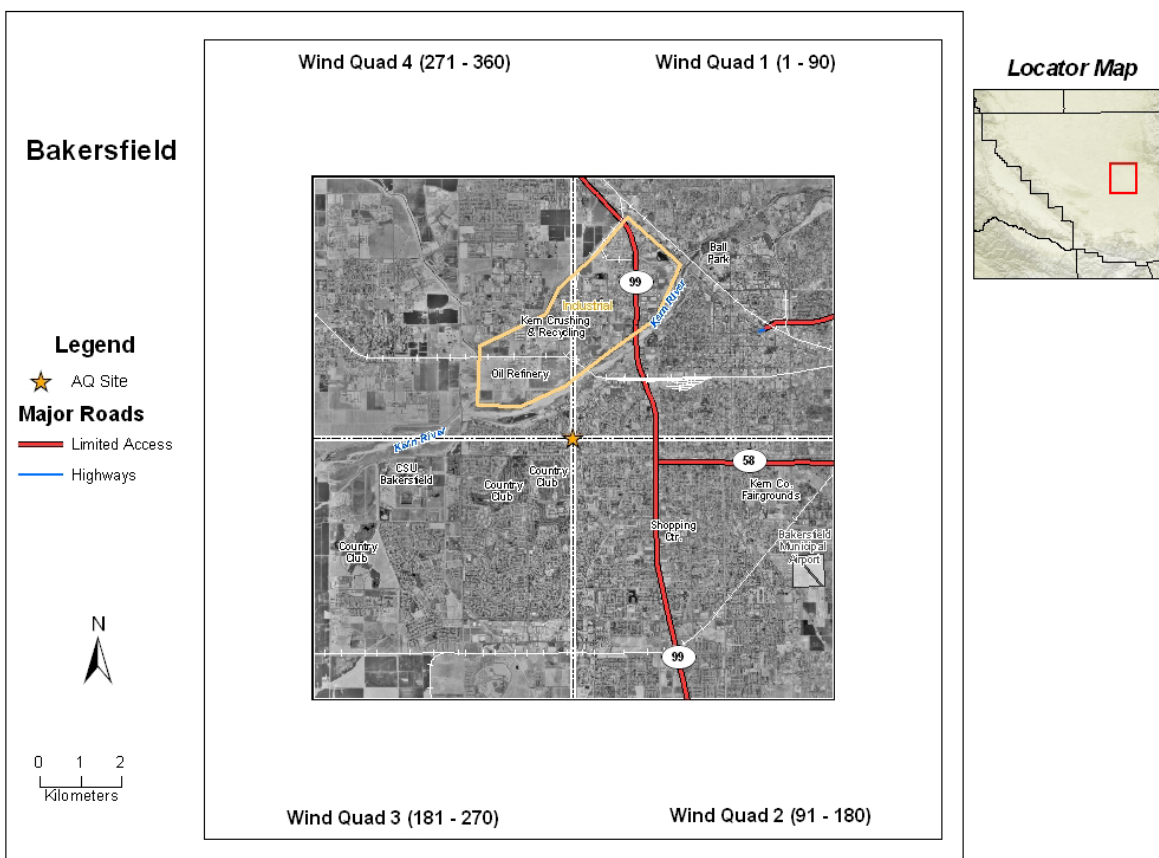
Figure 2-2. Map of the 10-km by 10-km area surrounding the Bakersfield California Avenue ambient monitoring site.

<u>*San Jose Fourth Street*</u>

The San Jose Fourth Street site is located in the center of a heavily populated urban area. Large, heavily traveled freeways occupy all quadrants. The site itself is surrounded on all sides by state highways and urban interstates (Figure 2-3).

Wind Quadrant 1 (1°–90°, Northeast) – Two heavily traveled freeways, U.S. Highway 101 and Interstate 680, run parallel in Quadrant 1. The land use throughout the quadrant appears to be a mix of residential and small business/commercial areas. Three golf courses and numerous parks are scattered across the quadrant, interspersed with residential areas and shopping malls. San Jose Medical Center is about 1 km east-northeast of the monitoring site.

Wind Quadrant 2 (91°–180°, Southeast) – San Jose State University is about 0.5 km southeast of the monitoring site. Another major freeway, Interstate 280, is about 1 km farther southeast; Interstate 280 is crossed by two major thoroughfares in this quadrant, State Highways 101 and 87. The residential/commercial area south of the University and Interstate 280 gives way to a small industrial/commercial area served by numerous railroad spurs. A long series of parks follows Coyote Creek along a line southeast through the quadrant. The area northeast of the creek appears to be A mixed residential and small business/commercial area that includes a small commercial airport.

Wind Quadrant 3 (181°–270°, Southwest) – The area about 1 km southwest of the monitoring site is small business/commercial; about 1.5 km from the site is the San Jose Arena. The remainder of the quadrant is largely residential with some business/commercial areas, including another small college, three hospitals, and several large shopping centers.

Wind Quadrant 4 (271°–360°, Northwest) – The area northwest of the monitoring site is mix of residential/small business/government until Interstate 880. San Jose International Airport lies just northwest of this freeway and dominates the land use south of U.S. Highway 101, with the exception of a largely residential area south of State Highway 82 (El Camino Real).

Figure 2-3. Map of the 10-km by 10-km area surrounding the San Jose Fourth Street ambient monitoring site.

Fresno First Street

The Fresno monitor is located about 1 km due east of a major thoroughfare, State Highway 41, in a largely residential area; some commercial development is situated along the highway. The surrounding area is shown in Figure 2-4.

Wind Quadrant 1 (1°–90°, Northeast) – The CRPAQS field survey shows the area immediately around the monitoring site is a residential area with a mix of homes, apartments, schools, local parks, and small businesses. Large sewage disposal ponds are situated about 2.5 km northeast of the site. About 0.5 km further east are the Fresno Yosemite International Airport and the National Guard Air Field, both of which fall mostly into Quadrant 2. California State University at Fresno (buildings, crops, and livestock areas) occupies a large area about 3.5 km northeast of the site. The remainder of Quadrant 1 is a mixture of residential/small business areas and a few agricultural fields.

Wind Quadrant 2 (91°–180°, Southeast) – This quadrant is largely residential with a small amount of agriculture, with the exception of the Fresno Yosemite International Airport and some commercial/small industry development south and southwest of it.

Wind Quadrant 3 (181°–270°, Southwest) – Quadrant 3 consists of residential/small business areas southwest of the monitoring site for about 5 km, up to the railroad line that parallels State Highway 99. Downtown Fresno lies in the lower part of the quadrant, bounded by State Highway 99 and two other state highways. Southwest of State Highway 99 is another smaller airport, Fresno-Chandler Airport, about 6.5 km from the site. Various croplands occupy the extreme southwest corner of the quadrant. Several ponding basins, part of area flood control, are scattered across all quadrants.

Wind Quadrant 4 (271°–360°, Northwest) – A large shopping center is situated about 1.5 km west of the monitoring site, on the west side of State Highway 41. The area north of this shopping center along the length of State Highway 41 on the west side is a commercial/small industry area. The majority of the quadrant is residential/small business. In addition to single family homes, and apartments, several mobile home parks are scattered across both Quadrants 3 and 4.
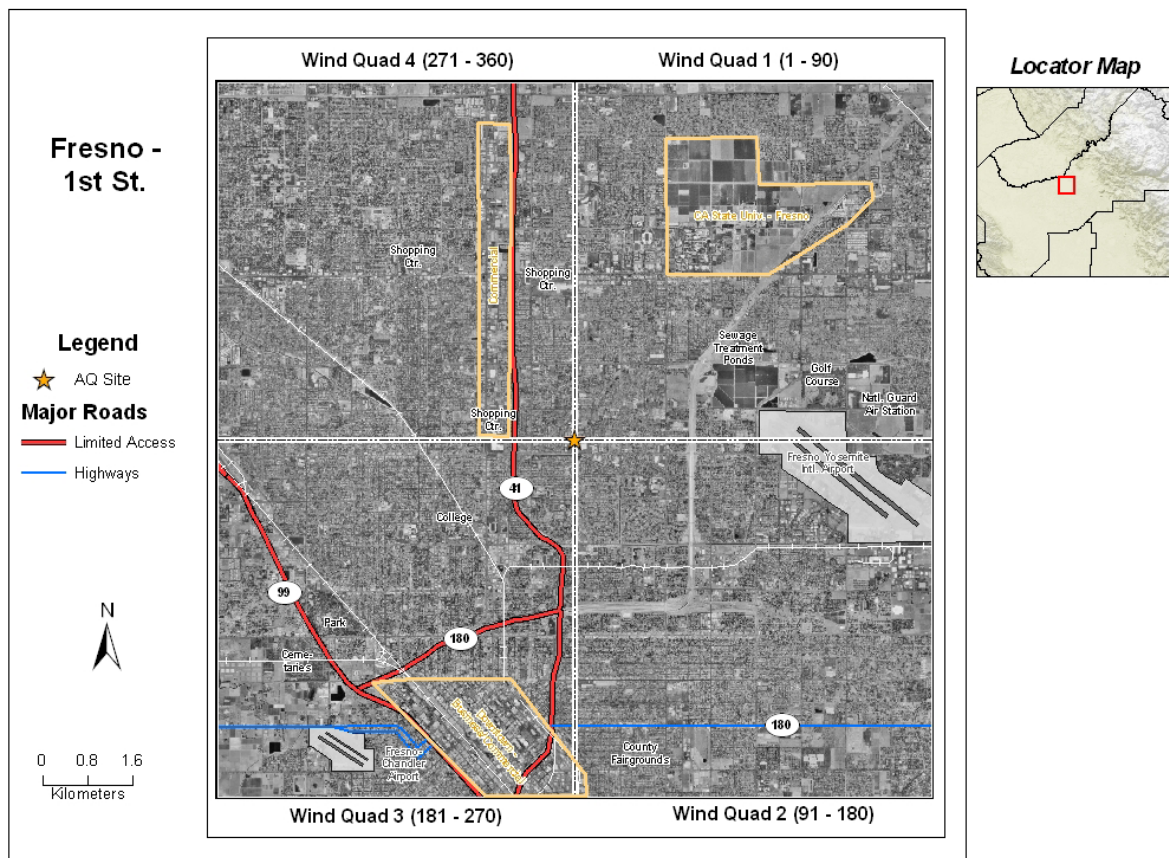

Figure 2-4. Map of the 10-km by 10-km area surrounding the Fresno First Street ambient monitoring site.

Sacramento Del Paso

Figure 2-5 shows that the area surrounding the Sacramento Del Paso monitoring site is predominantly suburban residential, along with several major freeways and a large Air Force base.

Wind Quadrant 1 (1°–90°, Northeast) – The CRPAQS field survey shows the area immediately around the monitoring site is a residential area with a mix of homes, apartments, schools, parks, and small businesses. The entire quadrant can be characterized the same way. There are several elementary and high schools with large and small campuses, and the American River College. Several parks are found in this quadrant, including the large regional American River Parkway along either bank of the American River in the southeast corner of the quadrant. Interstate 80 cuts across the northeast corner of the quadrant. A line of larger apartment buildings appear to follow along a surface street that parallels Interstate 80 to the southeast.

Wind Quadrant 2 (91°–180°, Southeast) – Quadrant 2 shows much the same character around the monitoring site and southeast to U.S. Highway 50. The residential area is peppered with schools, local parks, golf courses, and large parks along the American River. Mather Field, a former Air Force Base under conversion to a commercial park/general aviation airport, is in the southeast corner of the quadrant.

Wind Quadrant 3 (181°–270°, Southwest) – The area immediately around the monitoring site is mixture of homes, apartments, and schools. A large shopping center lies about 1 km due west of the site in Quadrant 3. The remainder of the quadrant is mostly residential, up to its outer boundaries. More of the American River Parkway runs along the southern end of the quadrant. California State University at Sacramento is in the southwest corner of the quadrant, between the river and U.S. Highway 50. North of the river, near Interstate 80 on the western boundary of the quadrant, is Cal Expo, the state fairgrounds.

Wind Quadrant 4 (271°–360°, Northwest) – The area immediately surrounding the monitoring site is a residential/small business neighborhood. The residential character, with schools and parks, continues from the site about 3 km to Business Interstate 80, which bisects the quadrant diagonally. McClellan Air Force Base (AFB) dominates Quadrant 4 north of Interstate 80. Additional residential area lies both east and southwest of the AFB. A large golf course, Haggin Oaks, and Del Paso Park separate the AFB from the residential area nearer to the site.
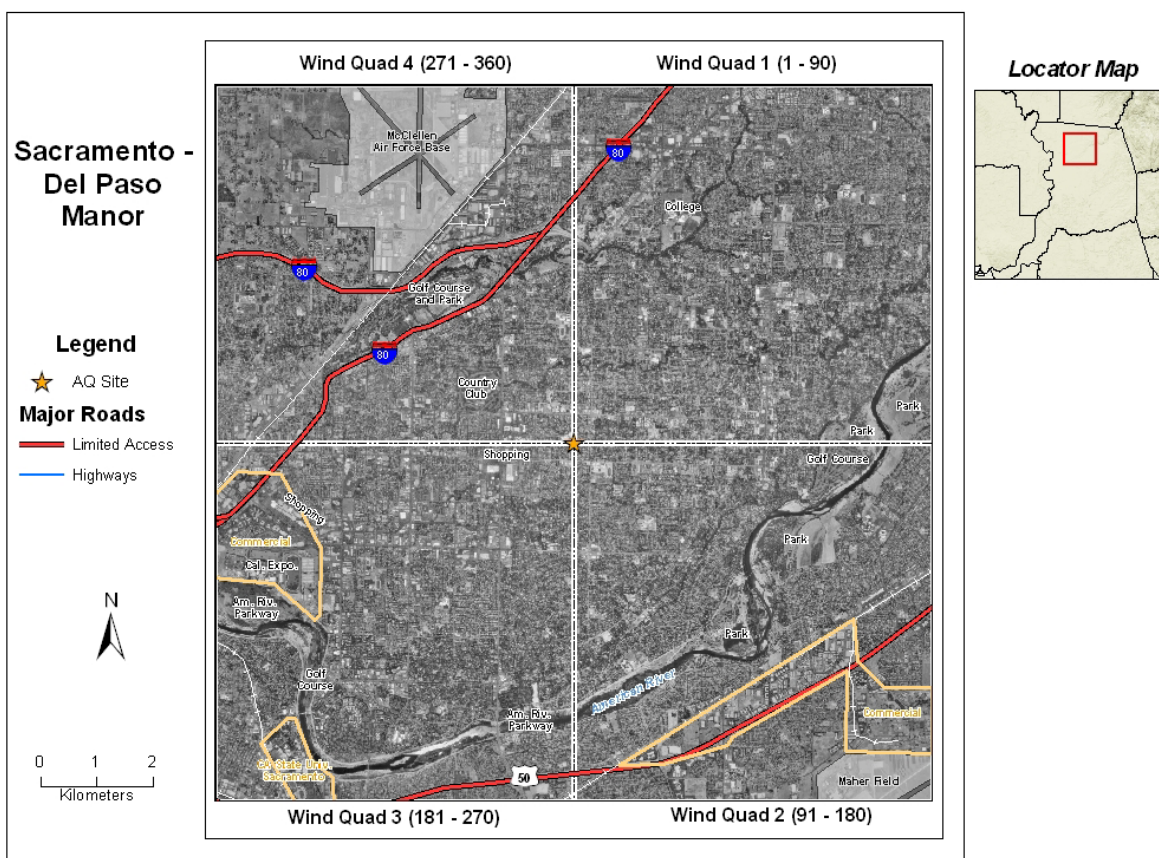
Figure 2-5. Map of the 10-km by 10-km area surrounding the Sacramento Del Paso ambient monitoring site.

2.1.2 Ambient Concentration Data

STI downloaded ambient concentration data for the five monitoring sites from the Central California Air Quality Studies (CCAQS) database, accessible on-line. **Table 2-1** summarizes the number of measurements available during the study period at each site by pollutant. SO_2 measurements were available only for Bakersfield; VOC measurements were available only for Bethel Island and Fresno; $PM_{2.5}$ chemistry measurements were available only for Bakersfield, Bethel Island, and Fresno. NO_x data for Bethel Island and San Jose were constructed from the sum of NO and NO_2 measurements. The ambient data sets for both $PM_{2.5}$ and VOCs were too small to perform separate weekday/weekend analyses. Diurnal profiles for these data are shown as notched box whisker plots in Section 3.2.

Table 2-1. Ambient data records available for analysis December 18, 2000–
January 24, 2001.

		Bakersfield	Bethel Island	Fresno	Sacramento	San Jose
NO_x –	All	1098	996	1095	1049	1096
	Weekday	776	720	773	739	774
	Weekend	276	230	276	266	276
CO –	All	366	391	388	368	387
	Weekday	251	276	273	258	272
	Weekend	92	92	92	88	92
$PM_{2.5}$ –	All	56	56	58		
SO_2 –	All	1125				
	Weekday	793				
	Weekend	284				
VOC –	All			47	33	

2.1.3   Meteorological Data

STI acquired hourly surface wind speed and direction data from the CCAQS data for
each site. The Bakersfield, Fresno, and Sacramento sites provided collocated meteorological
data. For Bethel Island, wind data were collected from the Brentwood 2-m tower, located about
9 km south of the monitoring site. Wind data for San Jose were collected from the San Jose
CIMIS 2-m tower, located 6 km southwest of the San Jose Fourth Street site.

For each site, the predominant wind direction and maximum hourly wind speed were
determined for each analysis hour (0500-0900 PST). We used these data to select the
appropriate emission inventory grid cells from which to calculate ratios for each hour.

2.2   EMISSION INVENTORY DATA

ARB provided hourly, gridded, speciated emission inventory data representing an
average winter weekday and weekend for the grid cells immediately surrounding the five
monitoring sites. The emission inventory contained hourly emission estimates for NO_x, CO,
SO_x, and VOCs. Emissions files were separated by major source category (i.e., area, non-road
mobile, on-road mobile, and point sources). SO_x was assumed to be equivalent to SO_2. VOC
data were speciated into individual hydrocarbons.

Speciated PM data, separated into 8 size bins and 16 species, were provide by UCD. The
size bins provided did not cut off at 2.5 µm. To estimate $PM_{2.5}$ mass, the first two size bins, plus
34% of the mass from the third size bin, were used. This calculation was based on assuming a
bimodal, lognormal size distribution with properties common to aerosols dominated by urban
and industrial sources (Omar et al., 2004).

3. RATIO COMPARISON

3.1   RATIO PROCESSING

STI calculated CO/NO_x, SO_2/NO_x, $PM_{2.5}/NO_x$, and VOC/NO_x ratios for ambient and emission inventory data. In each case, data were converted to units suitable for ratio comparison, and ratios were calculated for individual data points before averaging. Median pollutant ratios were compared to average ratios to help determine whether one of these statistics might be more suitable for use than the other. Median and average values were very similar and either would have been suitable. For simplicity, averages were used to support the analyses rather than medians.

3.1.1 CO, SO_2, and NO_x

Hourly ambient CO and NO_x data were available for the study period from all five sites. Only Bakersfield provided SO_2 data. Ambient CO/NO_x and SO_2/NO_x ppb ratios were calculated for each hour of each day. The ratios were then averaged by hour, predominant wind quadrant, and type of day (weekday or weekend). We treated the major holidays—Christmas and New Year's Day—as weekend days. Emission inventory data were converted to moles/hour, and ratios were calculated by grid cell by hour for a typical weekday and a typical weekend.

3.1.2   VOC

Ambient hydrocarbon data were collected in five-hour canisters at the Bethel Island and Fresno sites. We used data collected from 0500 through 1000 PST to calculate ppbC VOC/NO_x ratios. All hydrocarbons available in the emission inventory were used to calculate this ratio. The list of matched species is found in Appendix A. For the emission inventory, the ratios were calculated as molesC/hr VOC to moles/hr NO_x. Because the ambient measurements cover a five-hour period, we did not calculate ratios by wind quadrant. Emissions from all grid cells in the study area surrounding the sites (a 50-km by 50-km square) were used to calculate the emission inventory ratios. Also, not enough data were available to calculate an ambient ratio for weekend days; only weekday information was used.

3.1.3 $PM_{2.5}$

Ambient $PM_{2.5}$ chemistry data were available only in five-hour sampling periods (0500 through 1000 PST). $PM_{2.5}$ data from the emission inventory reflect only primary emissions. To perform valid ratio reconciliations, we estimated and removed the portion of ambient $PM_{2.5}$ mass that was attributed to secondary formation in the atmosphere. This calculation was performed in two ways: by subtracting the mass constituents associated with secondary aerosol (Equation 3-1) and by building the primary mass up from constituents associated with primary aerosol (Equation 3-2). The results of CRPAQS Task 6.2 showed that about 20% of organic carbon (OC) mass in $PM_{2.5}$ in this area is due to secondary formation. We compared ratios using both methods.

$$\text{Primary PM}_{2.5} = TotalMass - \left[(SO_4 + NO_3 + NH_4 + 0.2(OC*1.4)\right] \qquad \textbf{(3-1)}$$

$$\text{Primary PM}_{2.5} = 0.8(OC*1.4) + EC + 1.89*Al + 1.57*Si + 1.2*K + 1.4*Ca + 1.43*Fe \qquad \textbf{(3-2)}$$

Figure 3-1 shows the daily primary PM$_{2.5}$ derived by each method at the Bakersfield California Avenue site. **Figure 3-2** shows the same comparison for Bethel Island, and **Figure 3-3** shows it for Fresno First Street.

Figure 3-1. Comparison of primary PM$_{2.5}$ mass at Bakersfield calculated by adding primary constituents and subtracting secondary components.
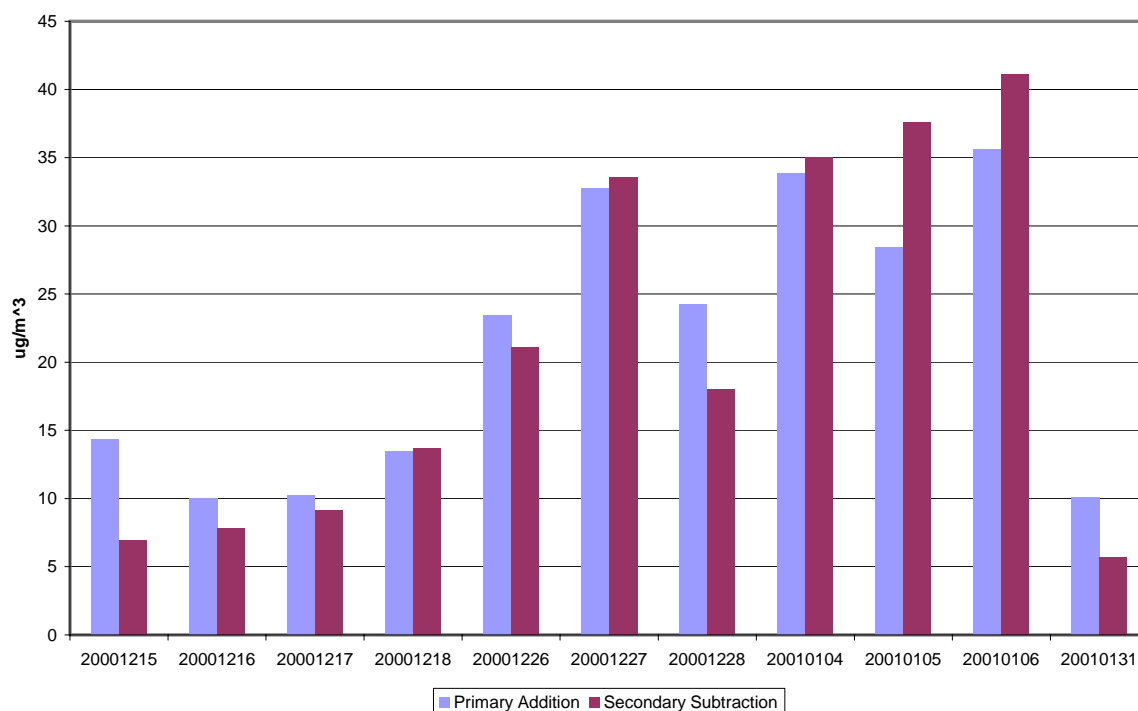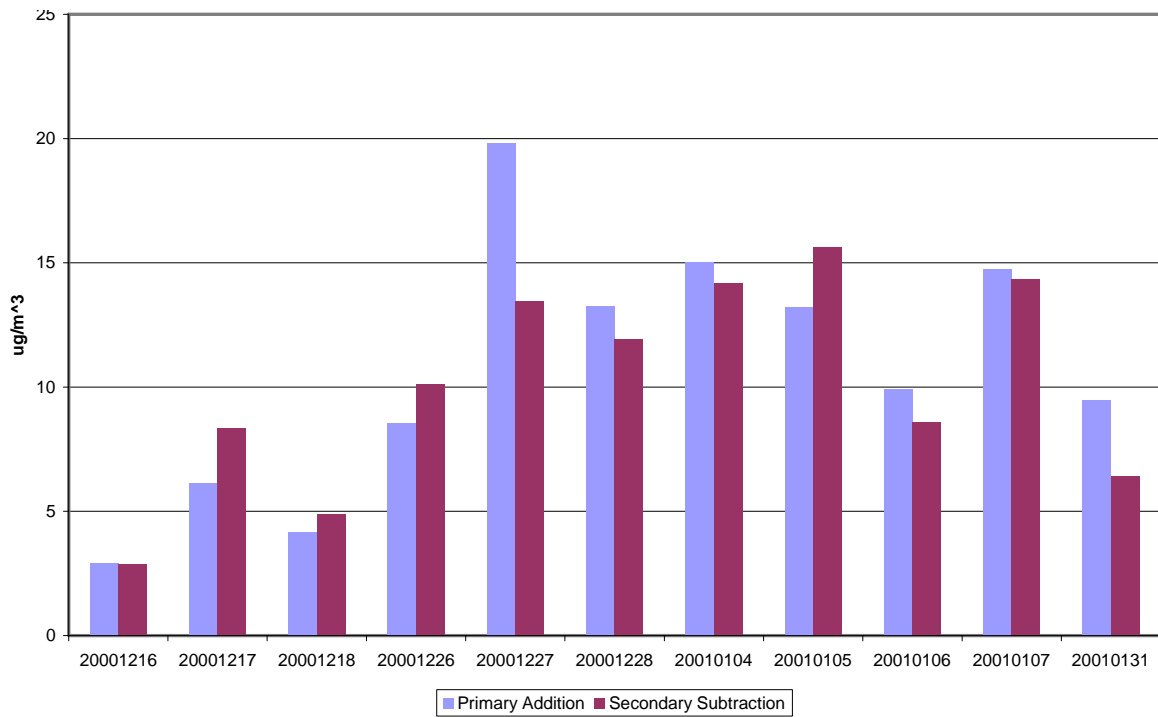
Figure 3-2. Comparison of primary PM$_{2.5}$ mass at Bethel Island calculated by adding primary constituents and subtracting secondary components.
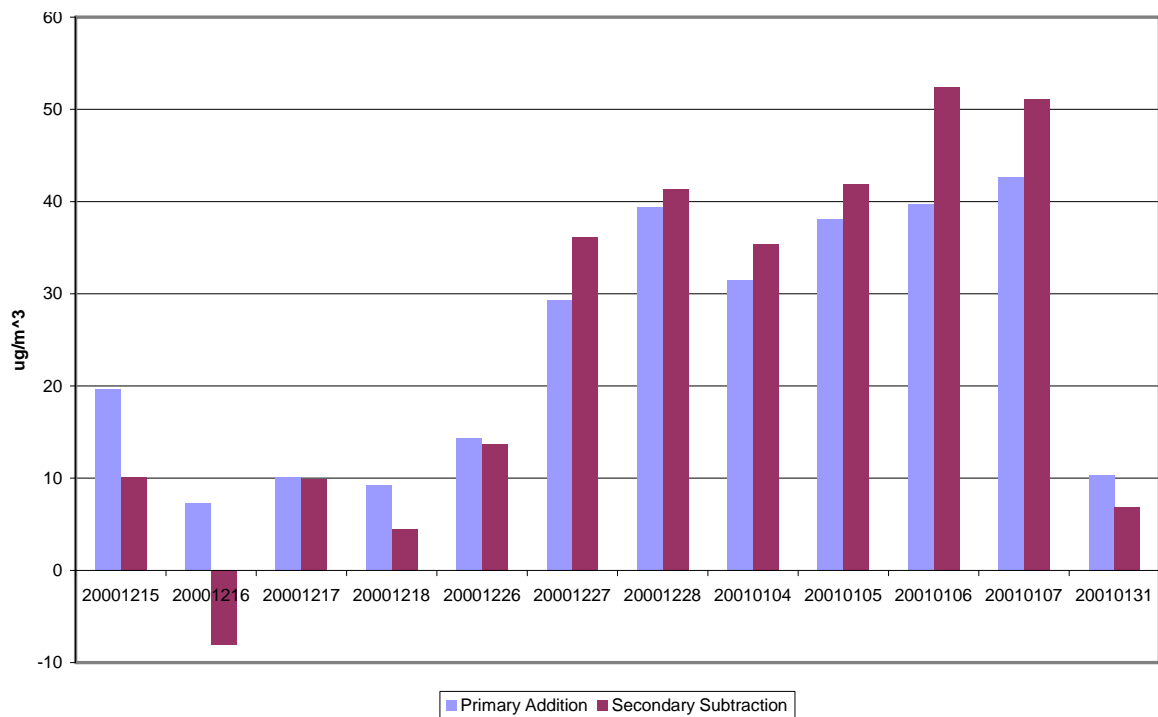

Figure 3-3. Comparison of primary PM$_{2.5}$ mass at Fresno First Street calculated by adding primary constituents and subtracting secondary components.

3.2 RESULTS

3.2.1 CO/NO$_x$ Ratios

CO/NO$_x$ ratios were computed for all five sites. Overall, ambient ratios are 2–12 times higher than emission inventory ratios; largely urban sites are dominated by mobile sources and their ratios show the best comparison. Weekday ratios are more similar than weekend ratios, and late morning hours (0800-0900 PST) compare better than early morning hours (0500-0700 PST). The wind quadrant is also important. Removing elevated point sources from the analysis did not make a significant difference in the ratios.

Bakersfield California Avenue

Figure 3 4 depicts the ambient, emission inventory, and meteorological data used to compute CO/NO$_x$ ratios. Winds are predominantly light and from the east (Quadrants 1 and 2). CO emissions are mostly close to the site and dominated by mobile sources. However, Bakersfield is unique among the five sites in that its NO$_x$ emissions are dominated by area sources. Modeling results from the IMS95 project suggested that the spatial distribution of NO$_x$ emissions from area sources may be too concentrated in the Bakersfield area (Kleeman et al., 2005).

Both ambient NO$_x$ and CO show high concentrations in the morning hours, satisfying the assumption of fresh emissions. The resulting ratios are shown in **Figure 3-5**. On average, the ambient CO/NO$_x$ ratios are 6.4 times higher than the emission inventory ratios. The ratios are closest from Quadrant 3, which has the least CO emissions. On weekend days, the ambient ratios are higher than on weekdays, but the emission inventory ratios are actually lower. The results suggest that NO$_x$ emissions estimates are too high or that CO emissions estimates are underrepresented in Bakersfield, particularly for area sources and on the weekends.

Bethel Island

The area surrounding the Bethel Island monitor is mostly rural. The map in **Figure 3-6** shows that CO emissions are sparse, and most of the large sources are several kilometers from the site. The lack of fresh emissions around the site makes reconciliation difficult. The ambient concentrations of NO$_x$ measured at Bethel Island are much lower than at the other sites. The resulting ratios are presented in **Figure 3-7**. Ambient CO/NO$_x$ ratios are four to six times higher at Bethel Island than at any other site in the study while the emission inventory ratios are about the same. The highest ambient ratios come from Quadrant 4, which shows persistent strong winds and few nearby emissions. Although a large portion of the NO$_x$ emission inventory within the grid domain around the Bethel Island site comes from elevated point sources, these sources do not have a significant impact on this analysis because greater than 90% of the emissions occur in grid cells near the periphery of the domain and are not included except in the strongest wind conditions. Overall, the ambient ratios are 12.6 times higher that the emission inventory ratios including elevated point sources and 11.6 times higher if elevated point sources are excluded.

Fresno First Street

As shown in the notched box whisker plots in **Figure 3-8**, ambient concentrations of CO and NO_x are high in the morning hours at the Fresno First Street monitoring site. The site is located in the center of the city surrounded by CO emission sources. Winds are predominantly from the east. Area and mobile sources account for almost all the CO emissions in the inventory. The calculated ratios are shown in **Figure 3-9**. On average for all circumstances, the ambient CO/NO_x ratio is about 2.8 times greater than the emission inventory ratio. The ratios are most similar in Quadrant 1; the ambient ratio is 1.8 times larger than the emission inventory ratio. In this quadrant, the emission inventory ratios are about twice as high as they are in the other quadrants. This quadrant also shows the highest emissions of both CO and NO_x.

Sacramento Del Paso

Figure 3-10 presents the ambient concentrations, emissions, and wind pattern used to calculate CO/NO_x ratios for the Sacramento Del Paso site. The winds are predominantly from the southeast (Quadrant 2) or the northwest (Quadrant 4). Inventory emissions are dominated by mobile and area sources for both CO and NO_x. Elevated point sources are not important. Ambient concentrations of both pollutants are high in the morning hours used in the study. **Figure 3-11** shows the calculated ratios. Overall, the ambient CO/NO_x ratios are two times higher than the ratios calculated from the emission inventory. Comparisons are closest in Quadrant 4 and in the late (0700-0900 PST) morning hours.

Figure 3-4. Bakersfield CO/NO$_x$ ambient, emissions, and meteorology data.
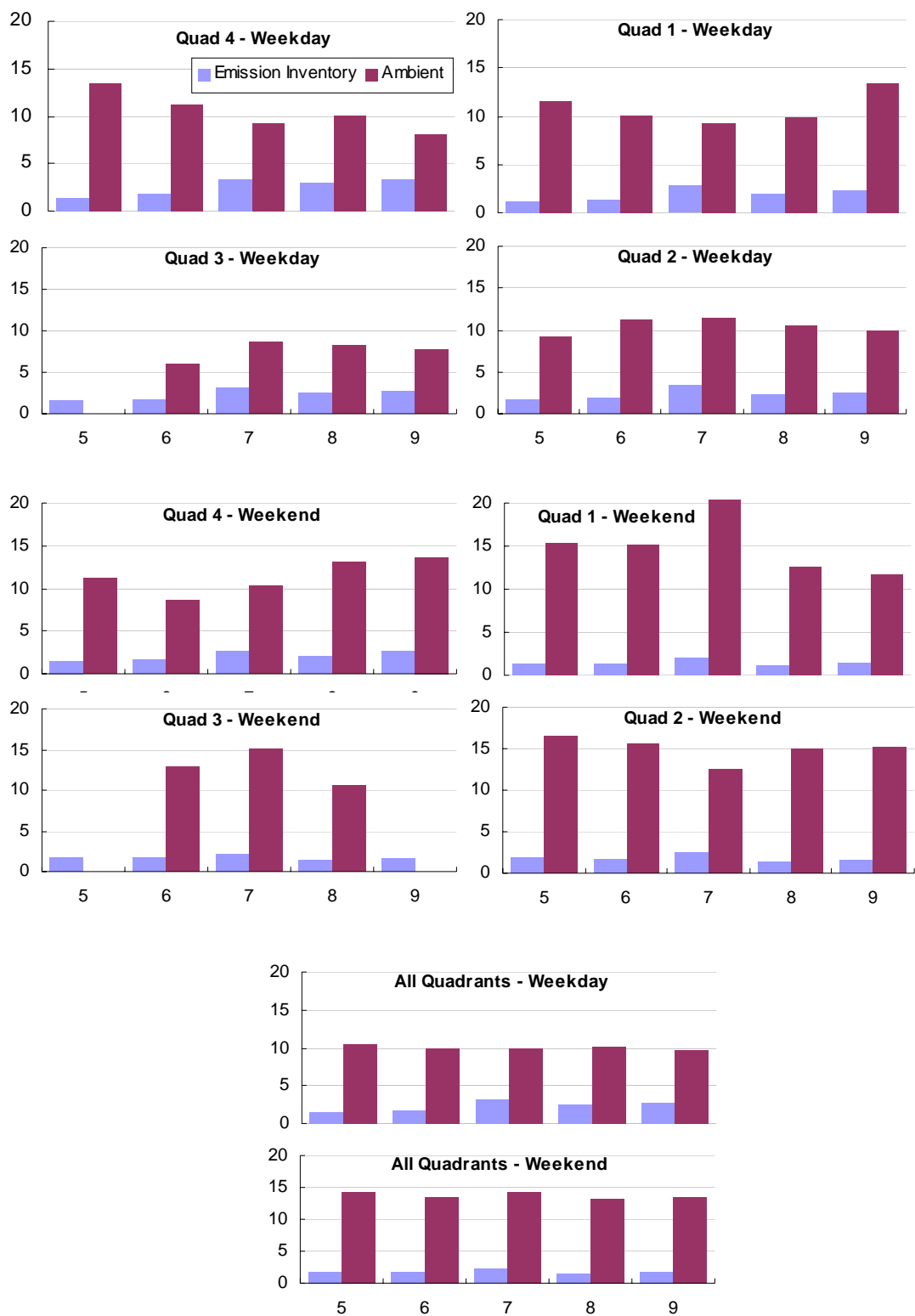
Figure 3-5. Bakersfield CO/NO$_x$ ratio comparisons by hour, quadrant, and day of week.
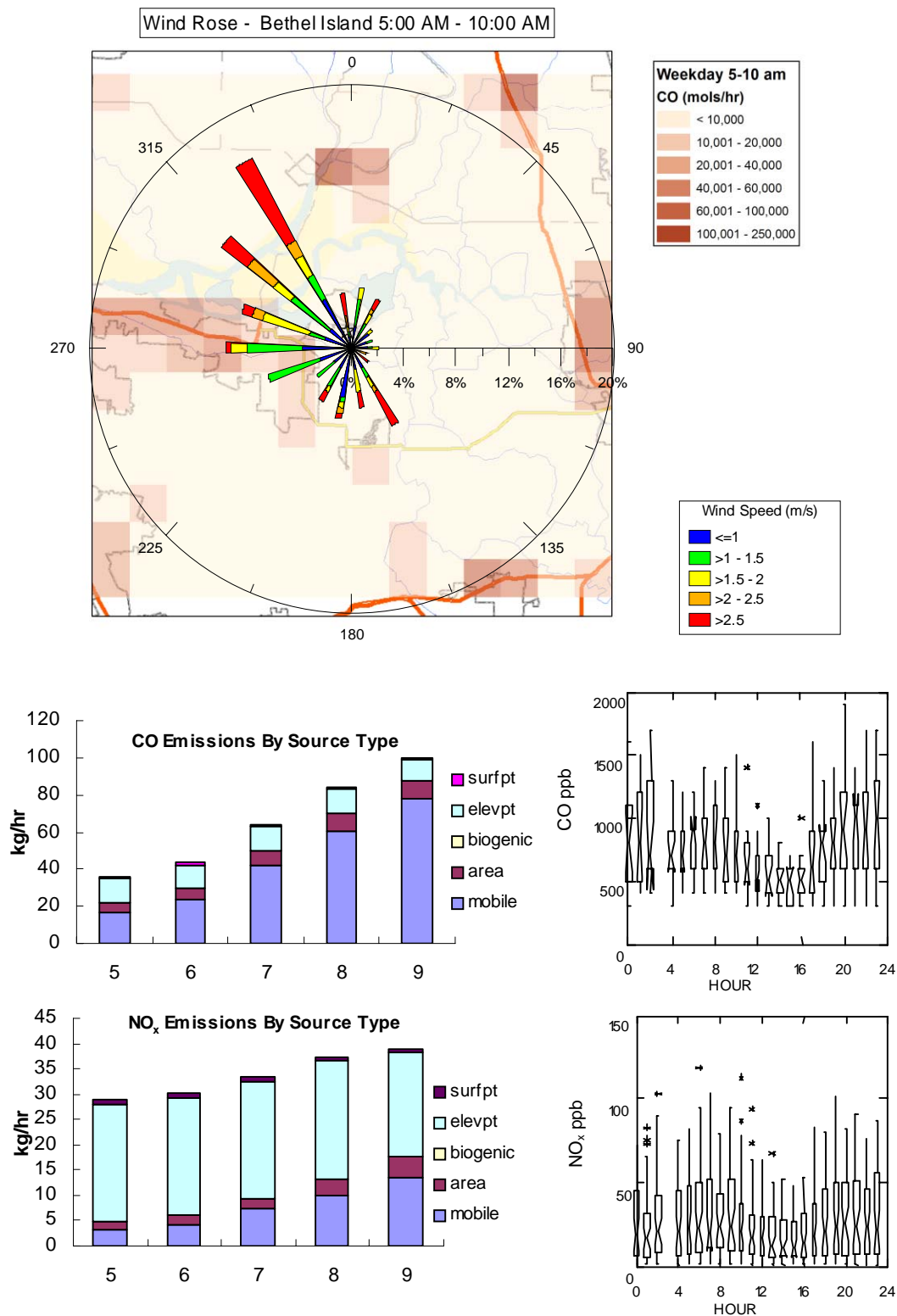
Figure 3-6. Bethel Island CO/NO$_x$ ambient, emissions, and meteorology data.
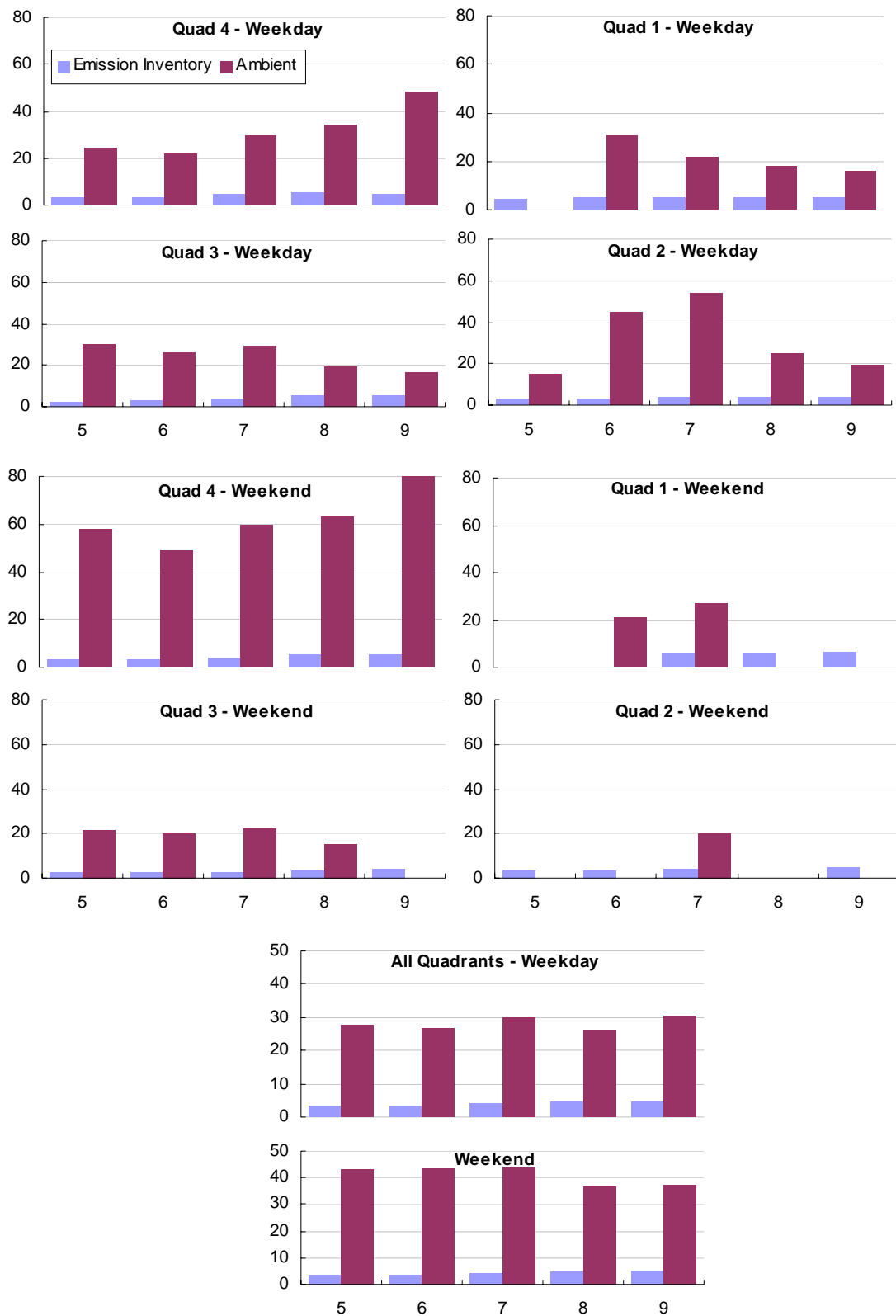
Figure 3-7. Bethel Island CO/NO$_x$ ratio comparisons by hour, quadrant, and day of week.
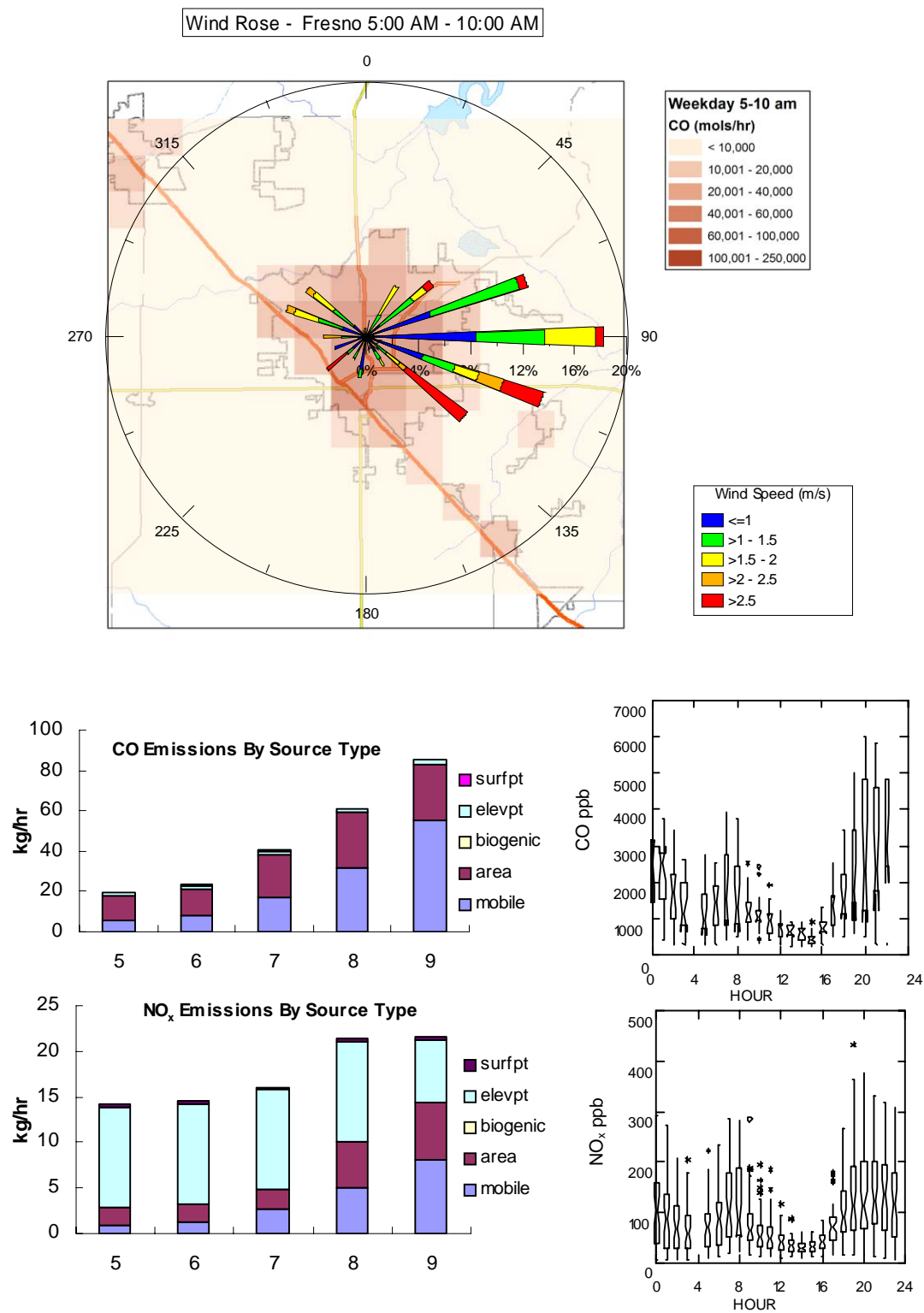
Figure 3-8. Fresno First Street CO/NO$_x$ ambient, emissions, and meteorological data..
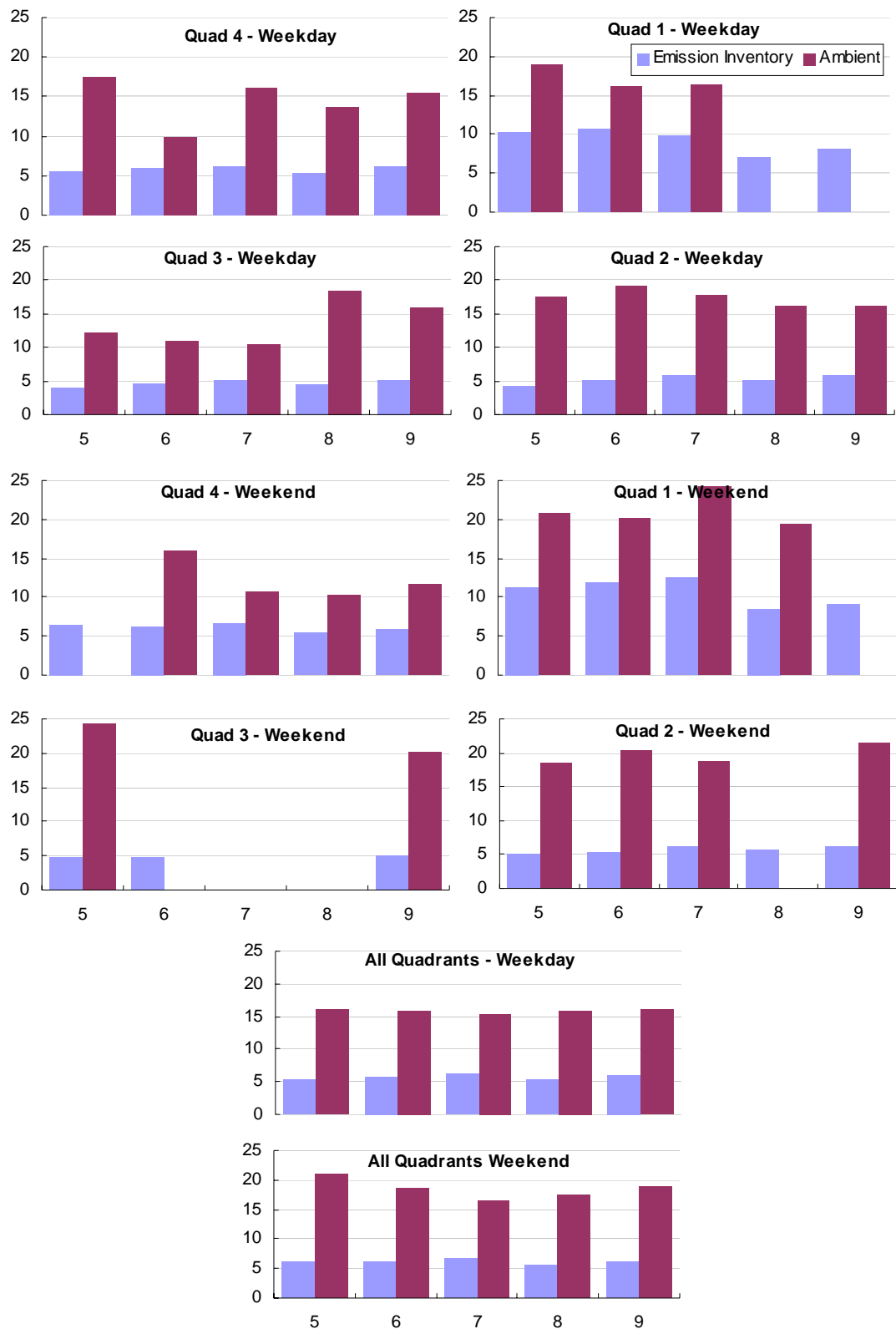
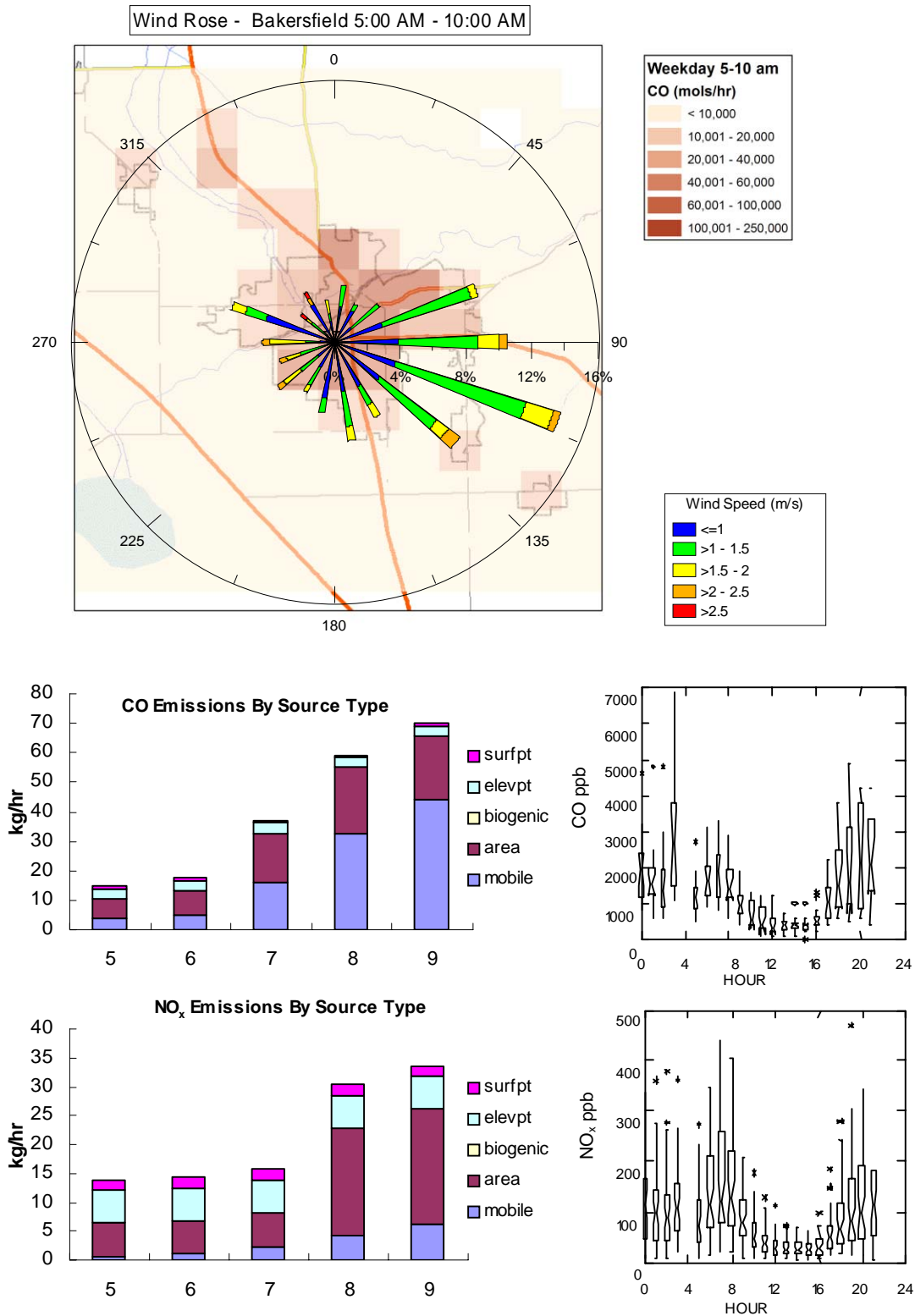Figure 3-9. Fresno First Street CO/NO$_x$ ratio comparisons by hour, quadrant, and day of week.
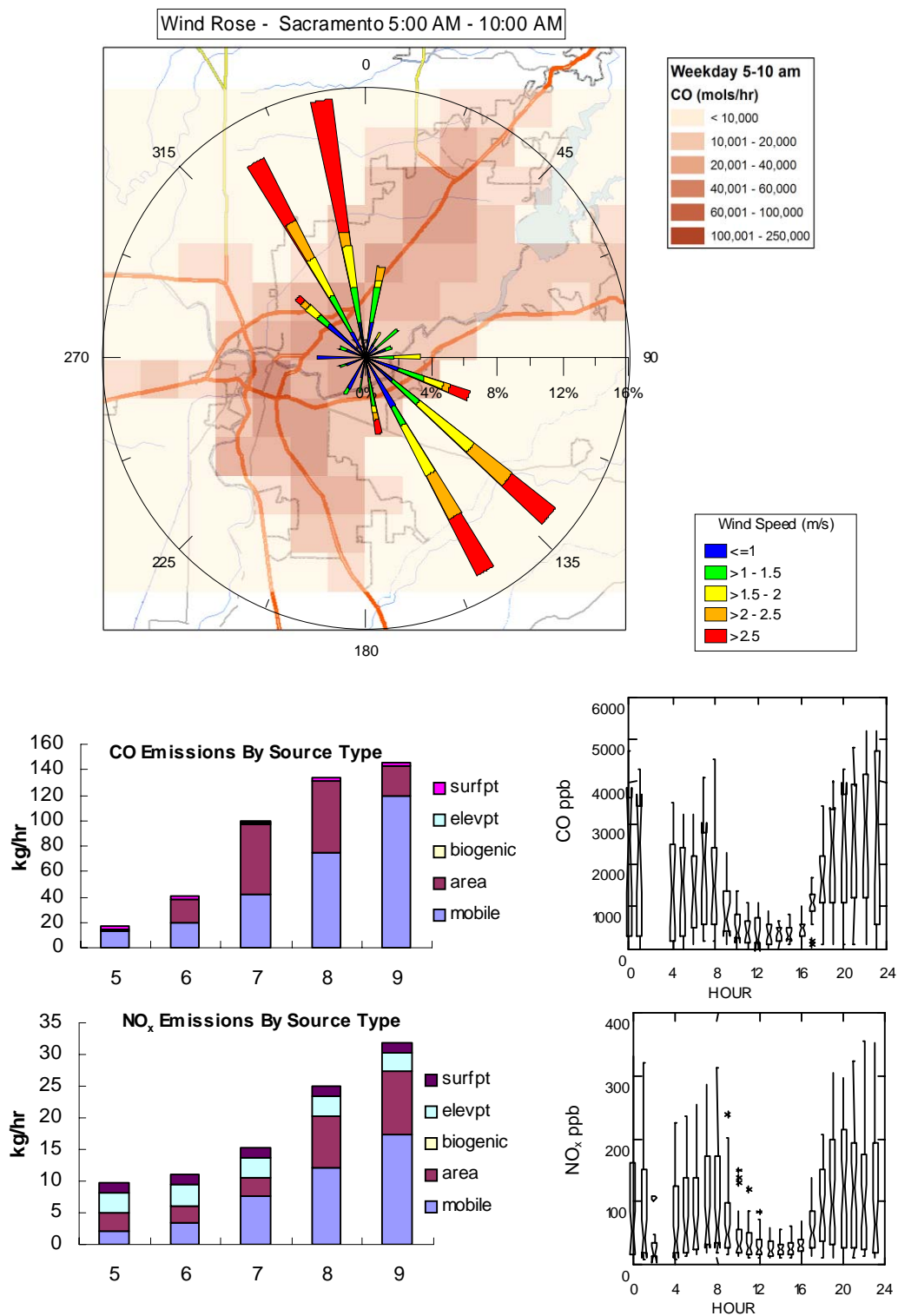
Figure 3-10. Sacramento CO/NO$_x$ ambient, emissions, and meteorology data.
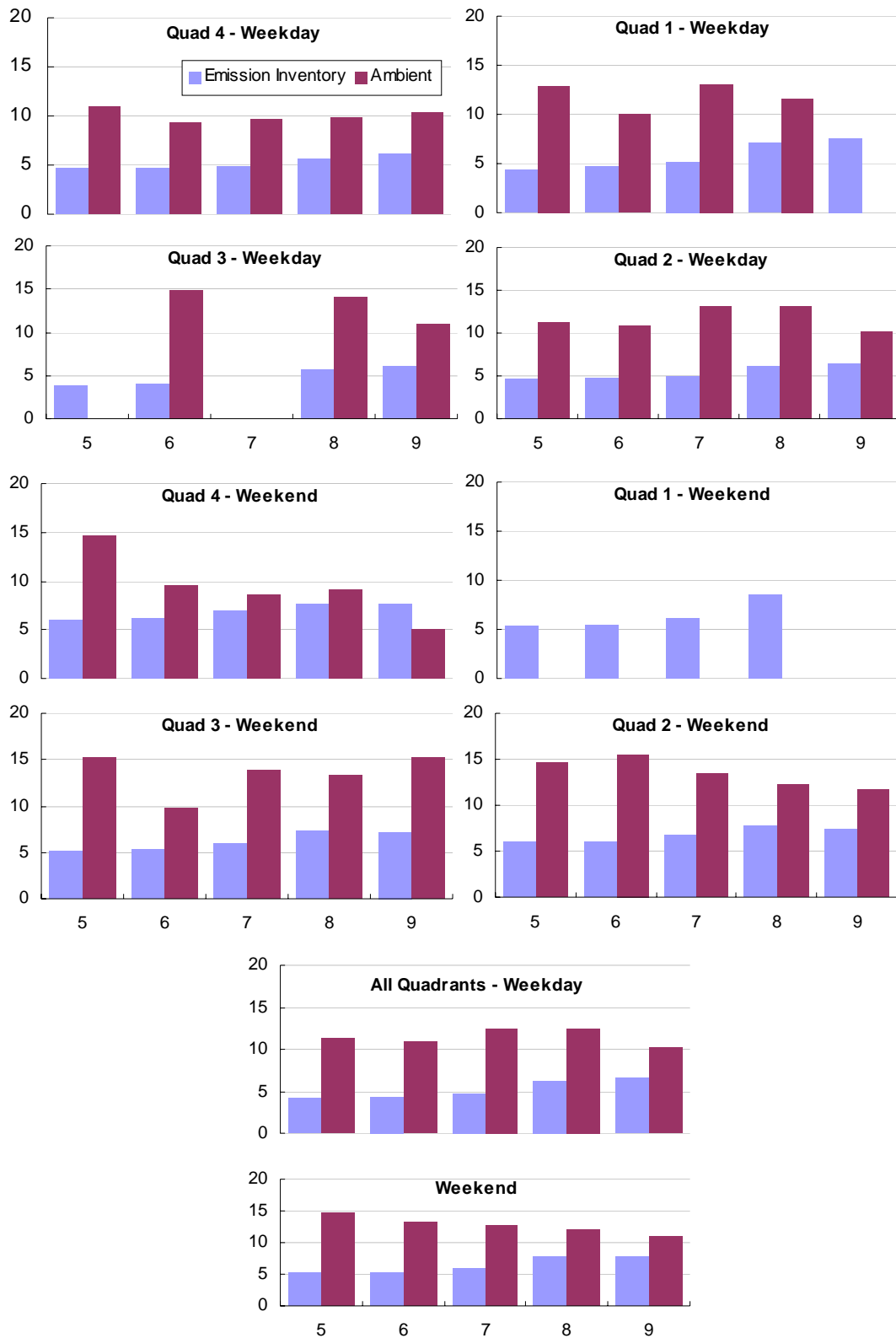
Figure 3-11. Sacramento CO/NO$_x$ ratio comparisons by hour, quadrant, and day of week.

San Jose Fourth Street

As shown in the stacked bar charts in **Figure 3-12**, San Jose Forth Street is the most mobile source-dominated of all the sites in this analysis. The site is within a few kilometers of several major freeways. NO_x and CO emissions are high during the morning hours studied. Winds are light and predominantly from the south, almost never from the northeast. **Figure 3-13** shows the CO/NO_x ratios for the San Jose site. Ambient ratios are about 2.3 times greater than the emission inventory ratios on average. Although the emission inventory ratios are fairly consistent across all variables (hour, quadrant, weekday/weekend), the ambient ratios vary, lowest on the weekdays and in Quadrant 2. These conditions produce the closest ratios. While the hour affects the calculated ratios, there is no apparent trend.

3.2.2 SO_2/NO_x Ratios

Only the Bakersfield California Avenue site produced the data required to perform the SO_2/NO_x ratio analysis. The stacked bar chart in **Figure 3-14** shows that the SO_2 emission inventory around the site is dominated by elevated point sources. However, SO_2 emissions are relatively low and ambient SO_2 concentrations are also low. The SO_2 notched box whisker plot in Figure 3-14 does not show a strong diurnal pattern. Thus, the assumption of fresh emissions does not necessarily hold. Despite this, we calculated SO_2/NO_x ratios, which are presented in **Figure 3-15**. For the early morning hours (0500-0700 PST), the emission inventory ratios are two to three times higher than the ambient ratios. Later in the morning (0800 through 1000 PST), the emission inventory ratios fall and become very similar to the ambient ratios. This trend is driven by the jump in NO_x emissions starting at 0800 PST (see Figure 3-14). Early morning (0500-0700 PST) NO_x emissions appear to be underrepresented in the emission inventory. Excluding elevated point sources from the analysis further improves the ratio comparison. Ratios do not differ substantially on weekdays versus weekends.
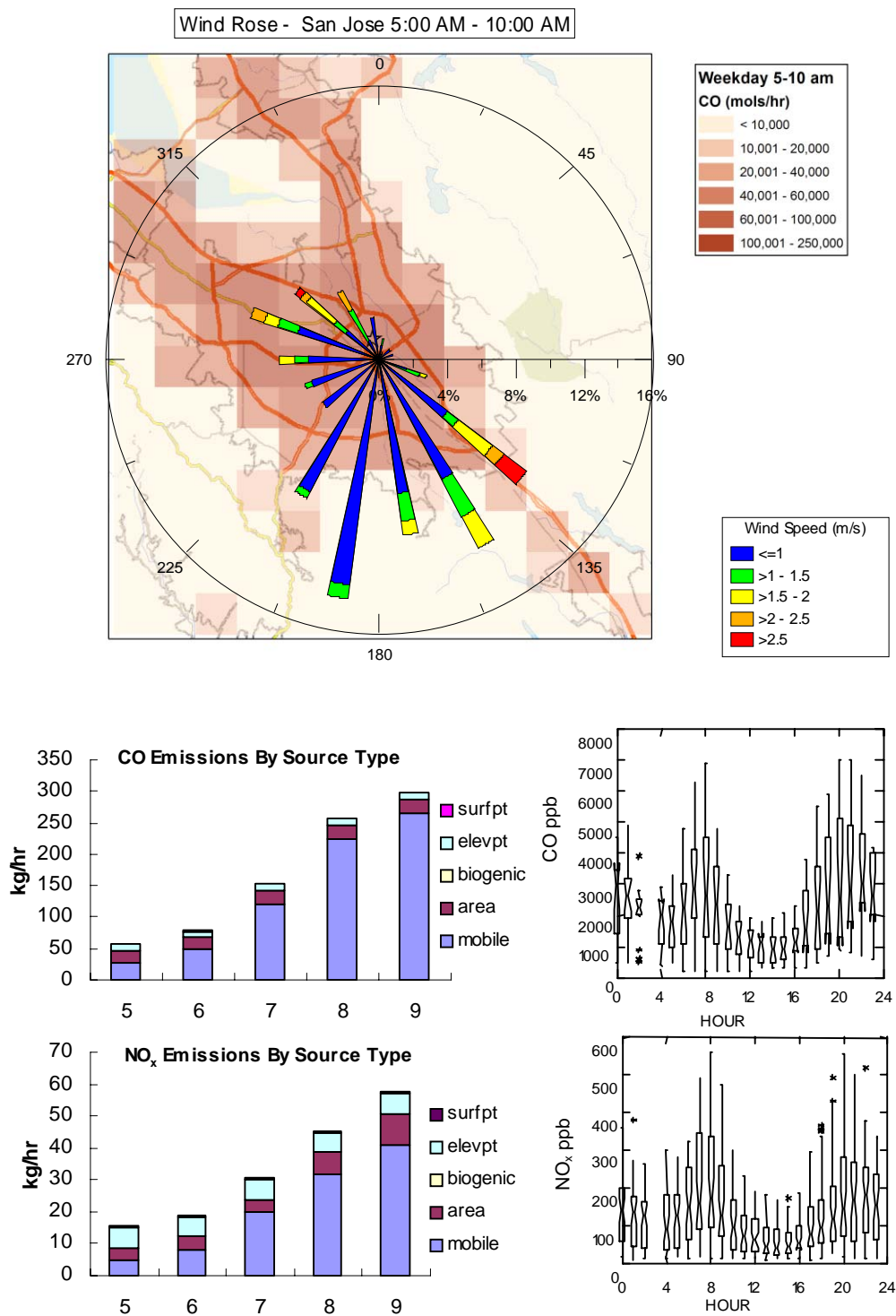
Figure 3-12. San Jose CO/NO$_x$ ambient, emissions, and meteorology data.
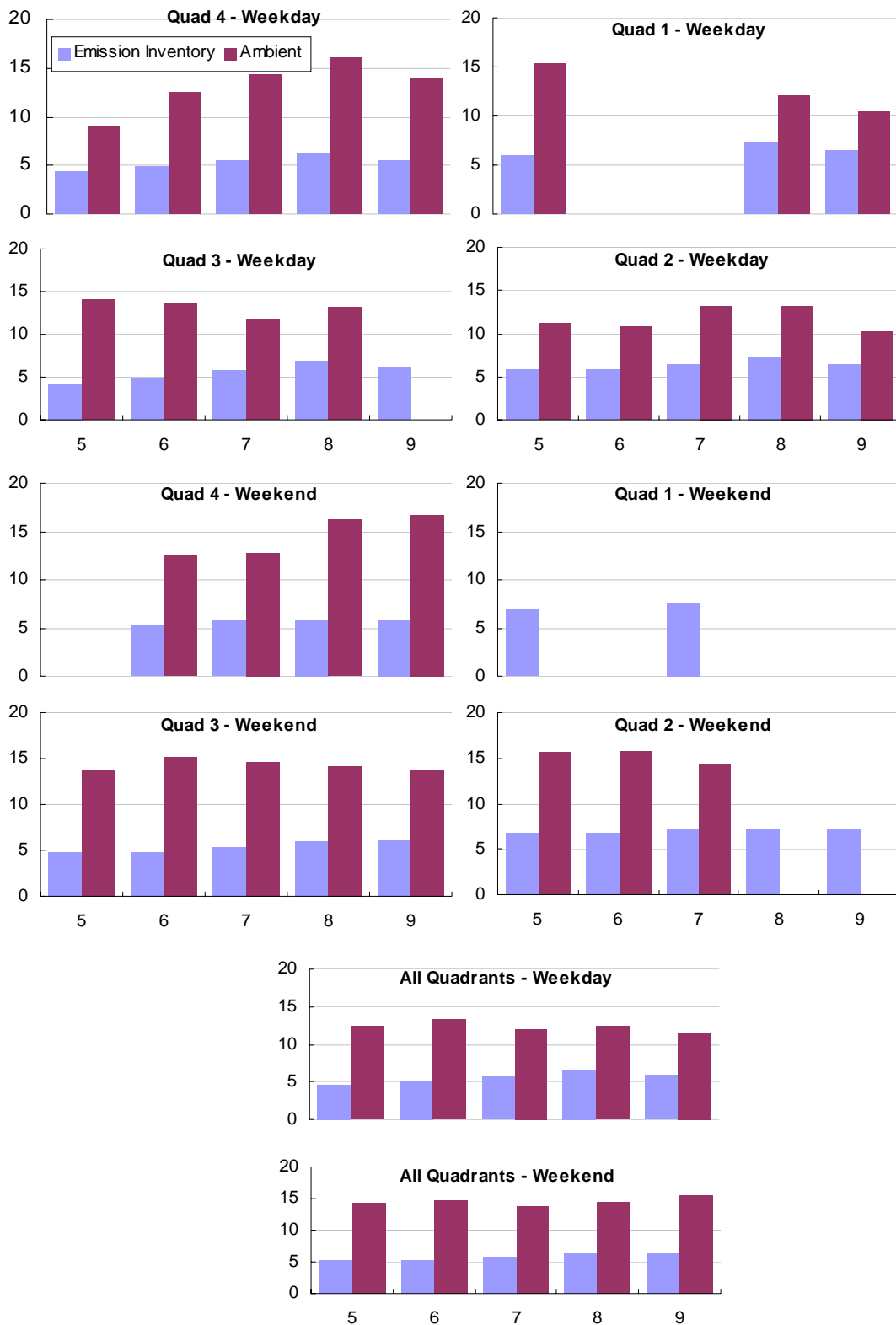
Figure 3-13. San Jose CO/NO$_x$ ratio comparisons by hour, quadrant, and day of week.
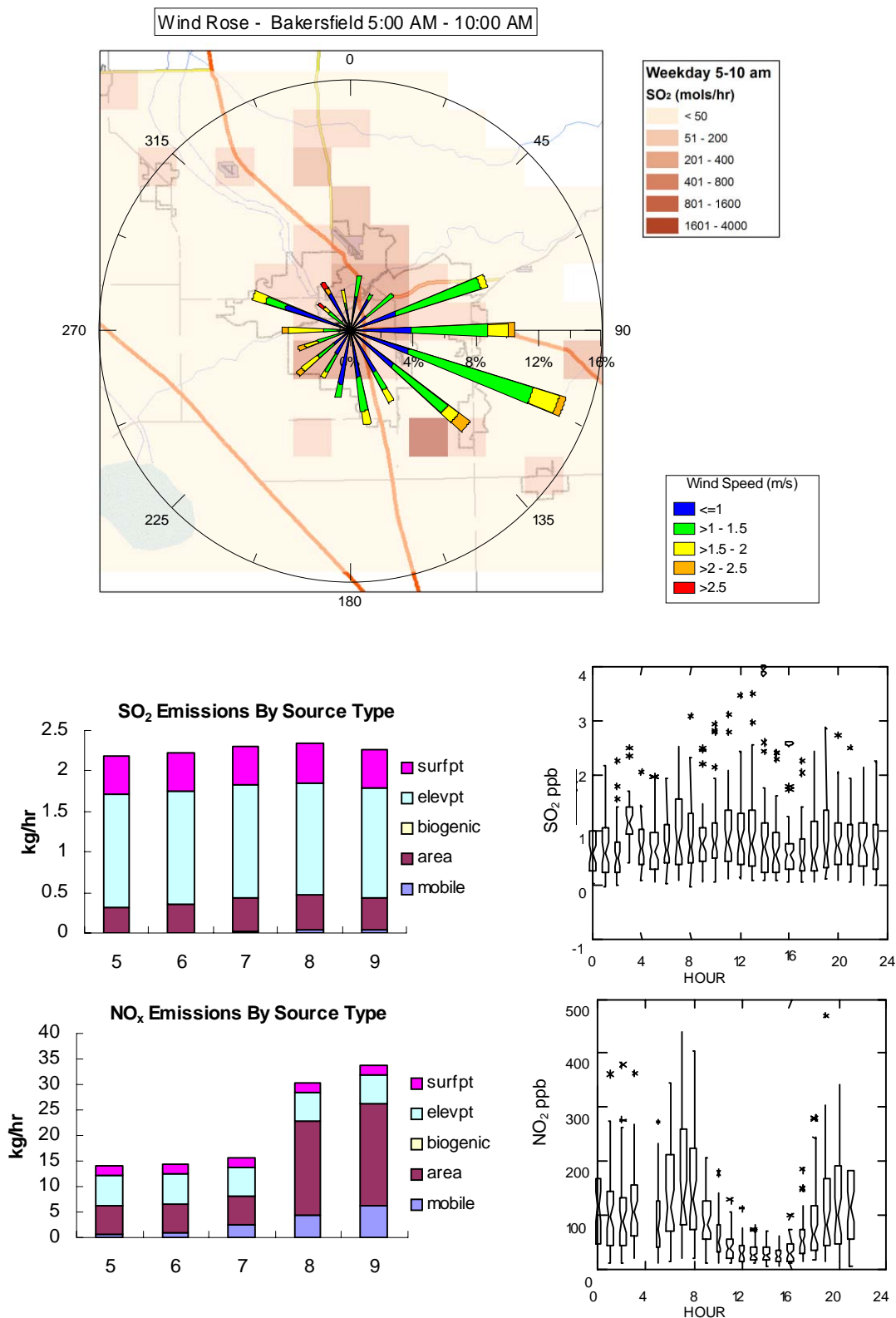
Figure 3-14. Bakersfield SO$_2$/NO$_x$ ambient, emissions, and meteorology data.
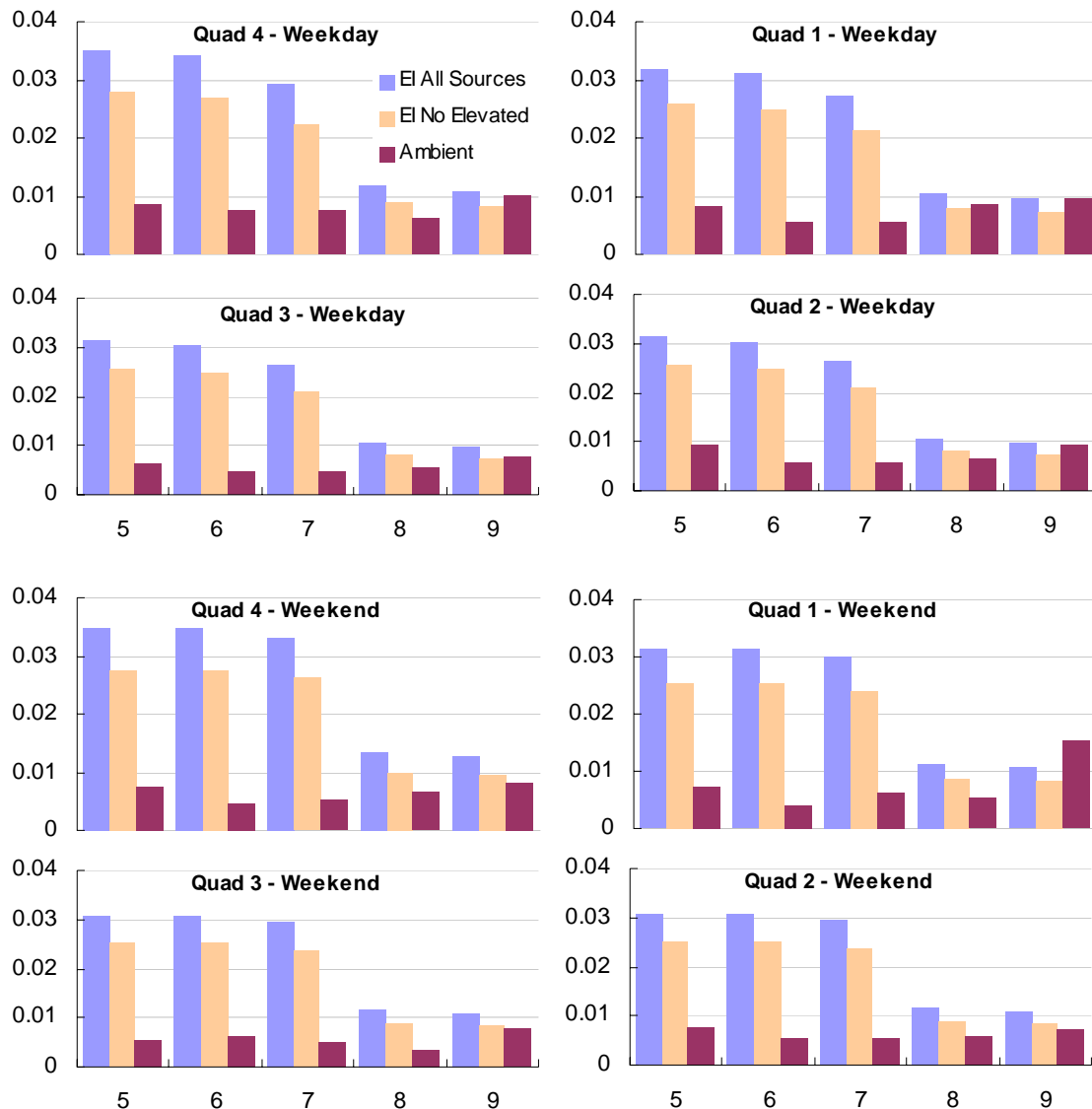
Figure 3-15. Bakersfield SO_2/NO_x ratio comparisons by hour, quadrant, and day of week, with and without elevated point sources.

3.2.3 VOC/NO$_x$ Ratios

VOC/NO$_x$ ratios were calculated for the Fresno and Bethel Island sites. Only limited data were available for the analysis. The ambient ratio is an average over the five-hour study period. Because of this, data were not segregated by wind quadrant. Only weekday data were used.

Bethel Island

Figure 3-16 summarizes the information used to calculate ambient and emission inventory VOC/NO$_x$ ratios for Bethel Island. The ambient-derived ratio is about 10 times greater than the emission inventory ratio. This analysis is confounded in Bethel Island by the relatively low emission rates in the surrounding areas.

The stacked bar charts in **Figure 3-17** show that the VOC emission inventory around the Fresno First Street site consists almost totally of area sources. The ambient and emission inventory ratios for Fresno are much better than those for Bethel Island. Averaging of the five-hour time period, the ambient VOC/NO_x ratio is 1.5 times higher than the emission inventory ratio. This comparison is the closest observed for VOC/NO_x in the Fresno area. The comparison is best in the early morning hours (0500-0600 PST).

3.2.4   PM$_{2.5}$/NO$_x$ Ratios

PM$_{2.5}$/NO_x ratios were computed for the Bakersfield, Bethel Island, and Fresno sites. For all three sites, the diurnal patterns of ambient PM$_{2.5}$ concentration do not suggest that PM$_{2.5}$ in the morning hours is not driven by fresh emissions. The analysis is further confounded by the additional uncertainty associated with estimating the fraction of ambient PM$_{2.5}$ mass that is primary in origin. Primary fractions were calculated using both secondary subtraction and primary addition.

For all three sites, the PM emission inventory is dominated by area sources. In the year-2000 county- and air basin-level emission inventories, PM$_{2.5}$ emissions predominantly originated from sources of fugitive dust (geologic material), combustion, and mobile sources (see **Figure 3-18**). Other analyses have shown that geologic material comprises a very small fraction of ambient PM$_{2.5}$ mass in the SJV during the winter and have concluded that emissions of PM$_{2.5}$ fugitive dust are likely being overestimated (Magliano et al., 1999).

Bakersfield

The PM$_{2.5}$/NO_x ratio for ambient data was about three times smaller than the average emission inventory ratio for the Bakersfield California Avenue site (see **Figure 3-19**). Both methods of determining primary ambient PM$_{2.5}$ yielded similar PM$_{2.5}$/NO_x ratios. The emission inventory may be overestimating emissions.

Bethel Island

Figure 3-20 shows the PM$_{2.5}$/NO_x ratios for the Bethel Island site. For the early morning hours (0500-0800 PST), the emission inventory ratios are about 6.5 times higher than the overall morning ambient ratio. However, for the last two morning hours (0800-1000 PST), the emission inventory ratios drop to only 2.3 times the ambient ratio. Over the entire morning, the average emission inventory ratio is 5.2 times greater than the ambient ratio. Both methods for determining primary ambient PM$_{2.5}$ yielded nearly identical total concentrations.

Fresno

For the Fresno First Street site, the emission inventory PM$_{2.5}$/NO_x ratios are strongly dependant on hour of day, ranging from 0.77 at 0500 PST to 0.2 at 0900 PST (see **Figure 3-21**). The overall morning ambient ratio is 0.09 by secondary subtraction and 0.13 by addition of primary components. The average emission inventory ratio is about 4.5 times higher than the ambient ratio. The ratio suggests that the PM$_{2.5}$ emission inventory may be overestimated, particularly in the morning hours.
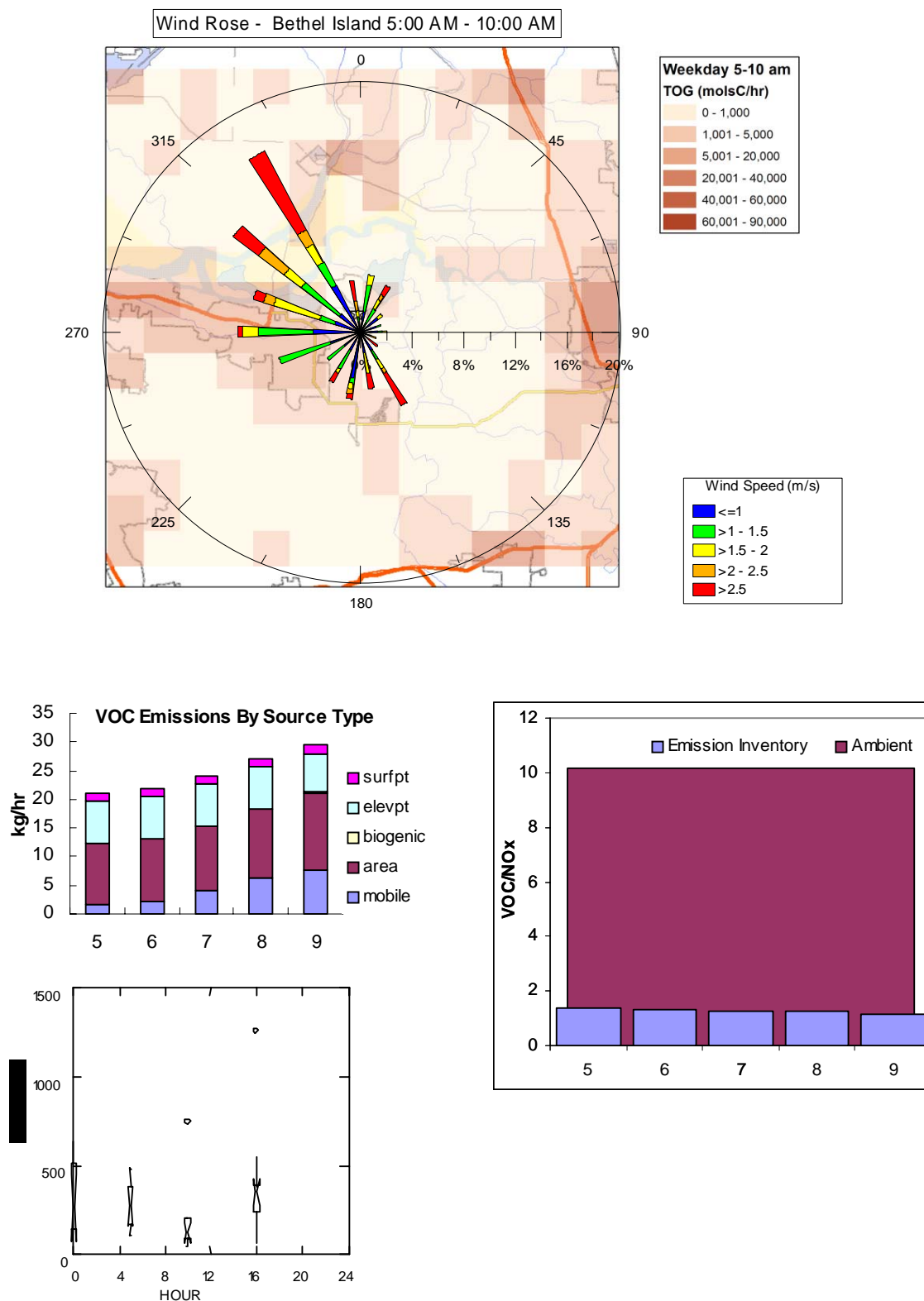
Figure 3-16. Bethel Island VOC/NO$_x$ ratio summary sheet. [4]

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[4] Gridded emissions of TOG are illustrated as a visual aid for comparison to the co-plotted wind rose (uppermost plot). Bar charts of VOC emissions represent only those individual VOC species (selected from the speciated TOG inventory) that are directly analogous to VOC species measured in the ambient air.
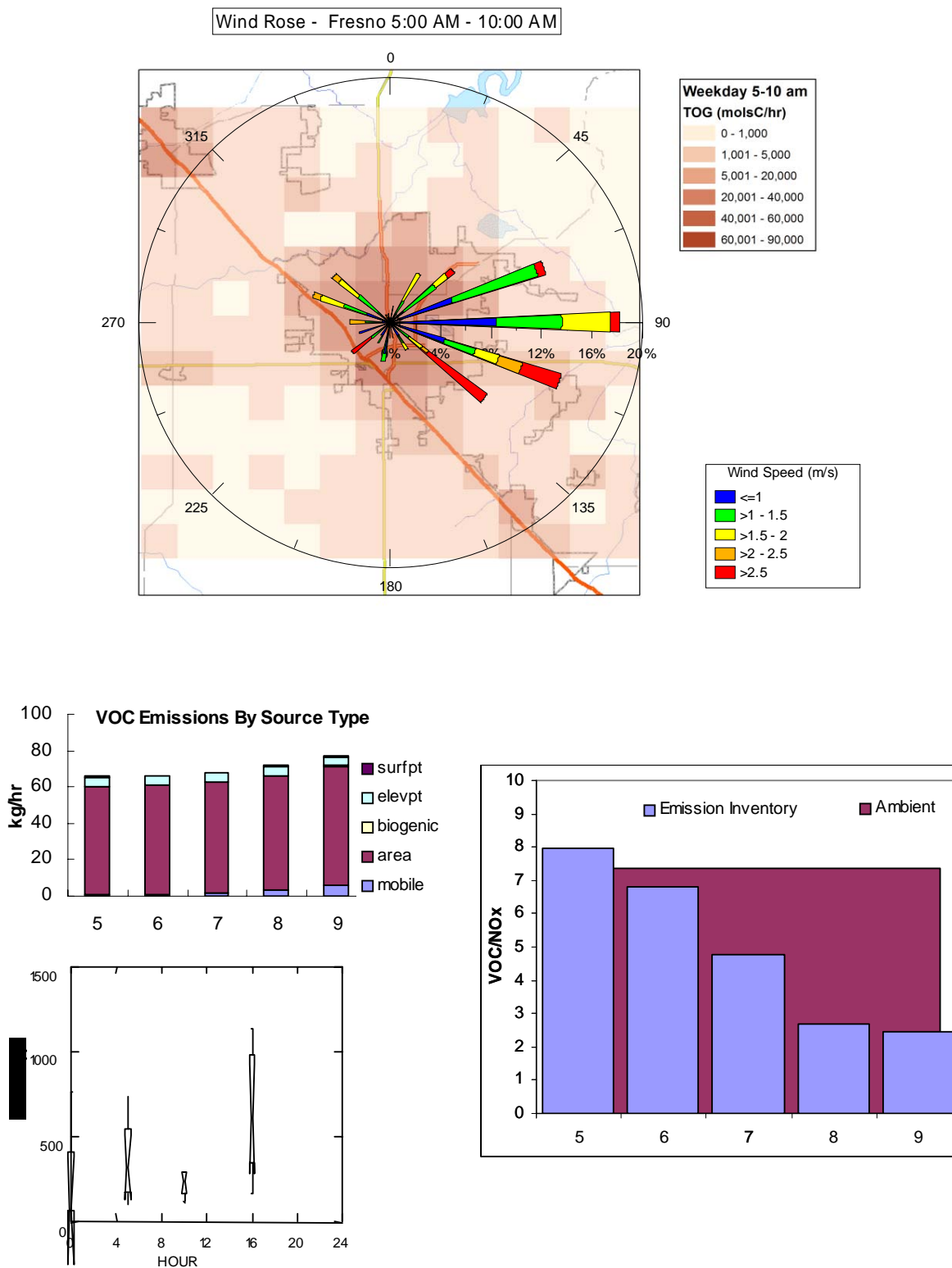
Figure 3-17. Fresno First Street VOC/NO$_x$ summary sheet.
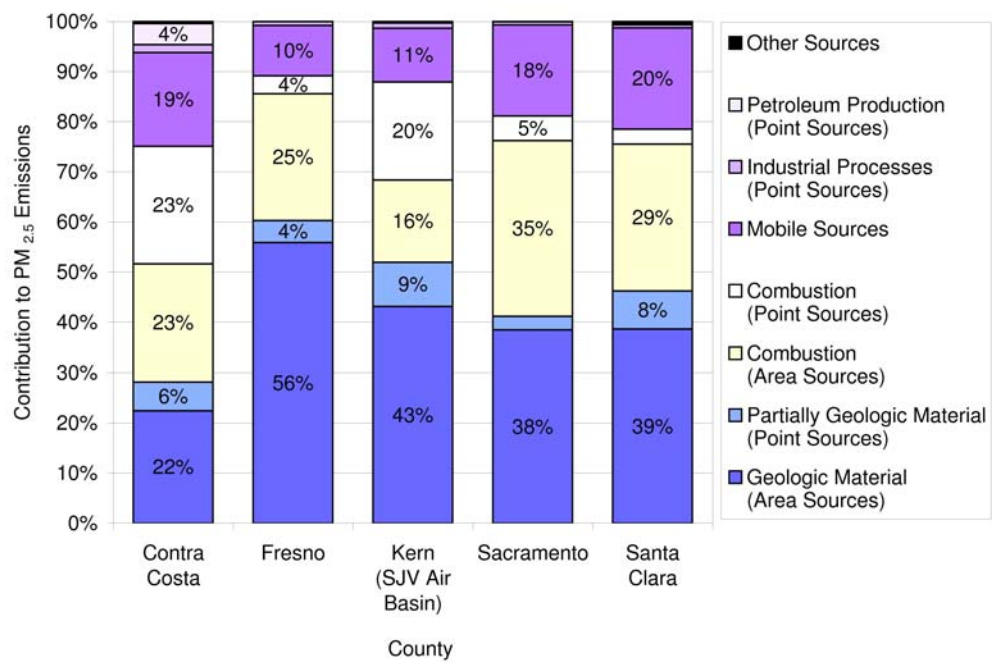
Figure 3-18. Distribution of year-2000 PM$_{2.5}$ emissions by source category (California Air Resources Board, 2005).
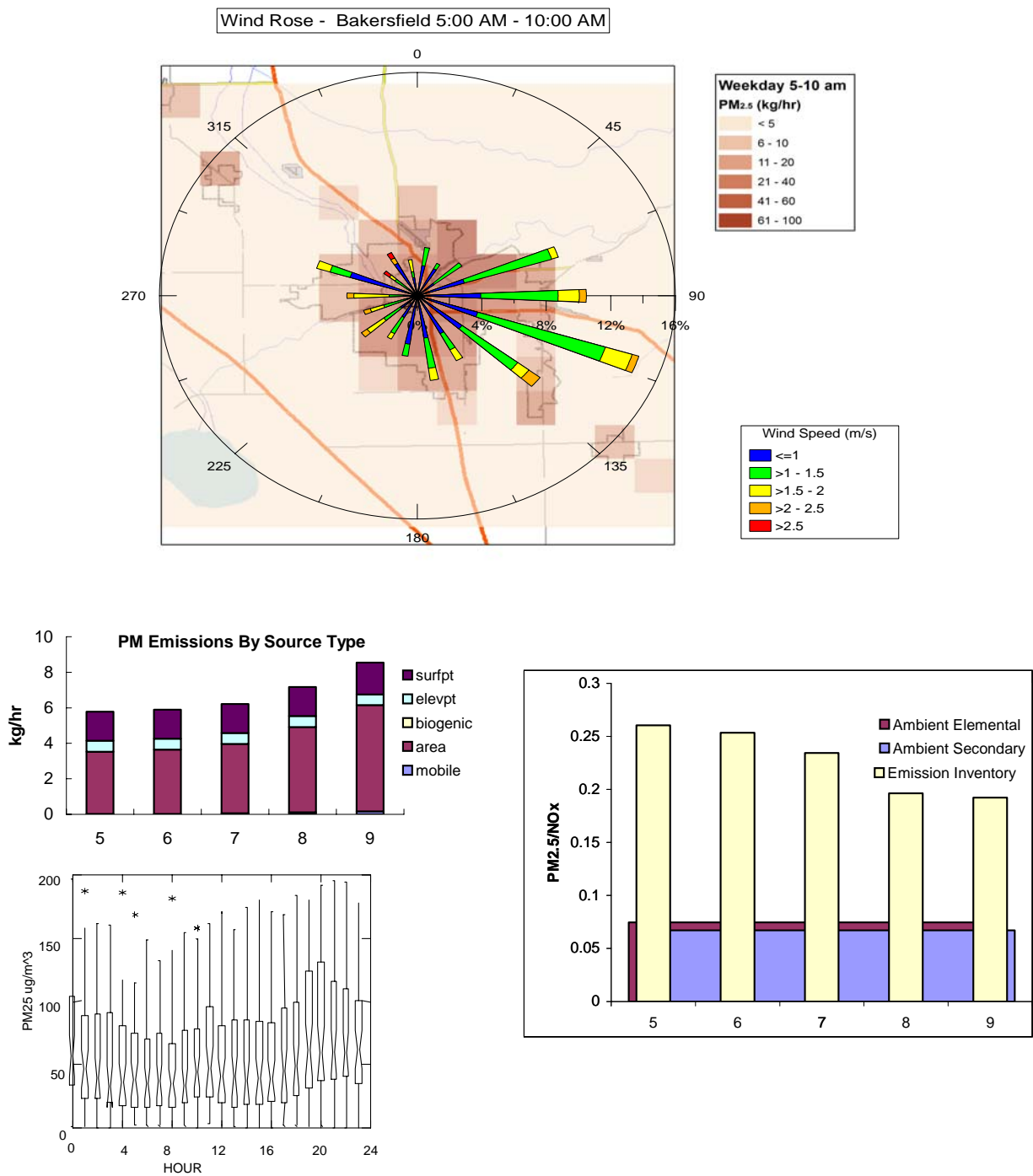
Figure 3-19. Bakersfield PM$_{2.5}$/NO$_x$ summary sheet.
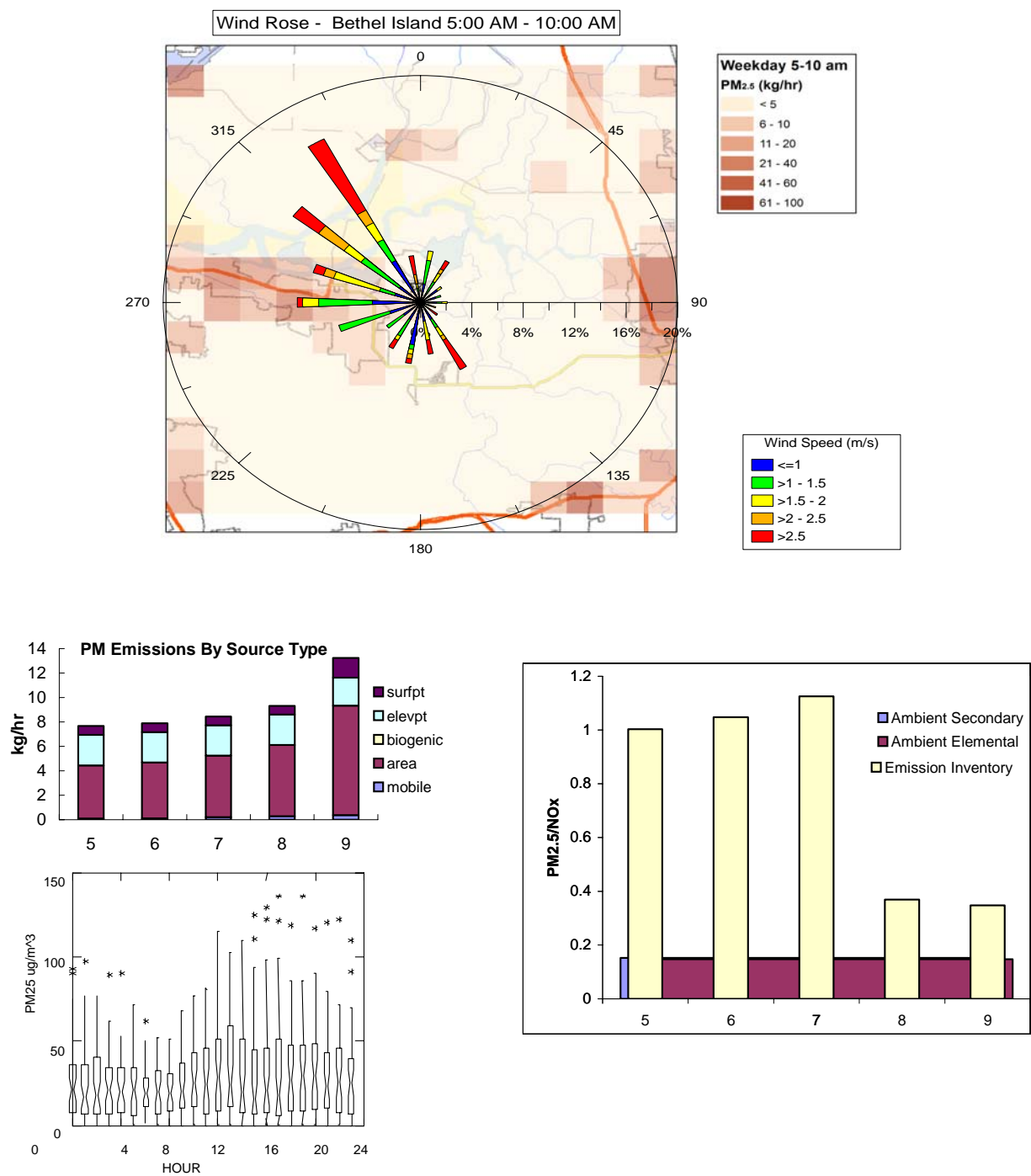
Figure 3-20. Bethel Island PM$_{2.5}$/NO$_x$ summary sheet.
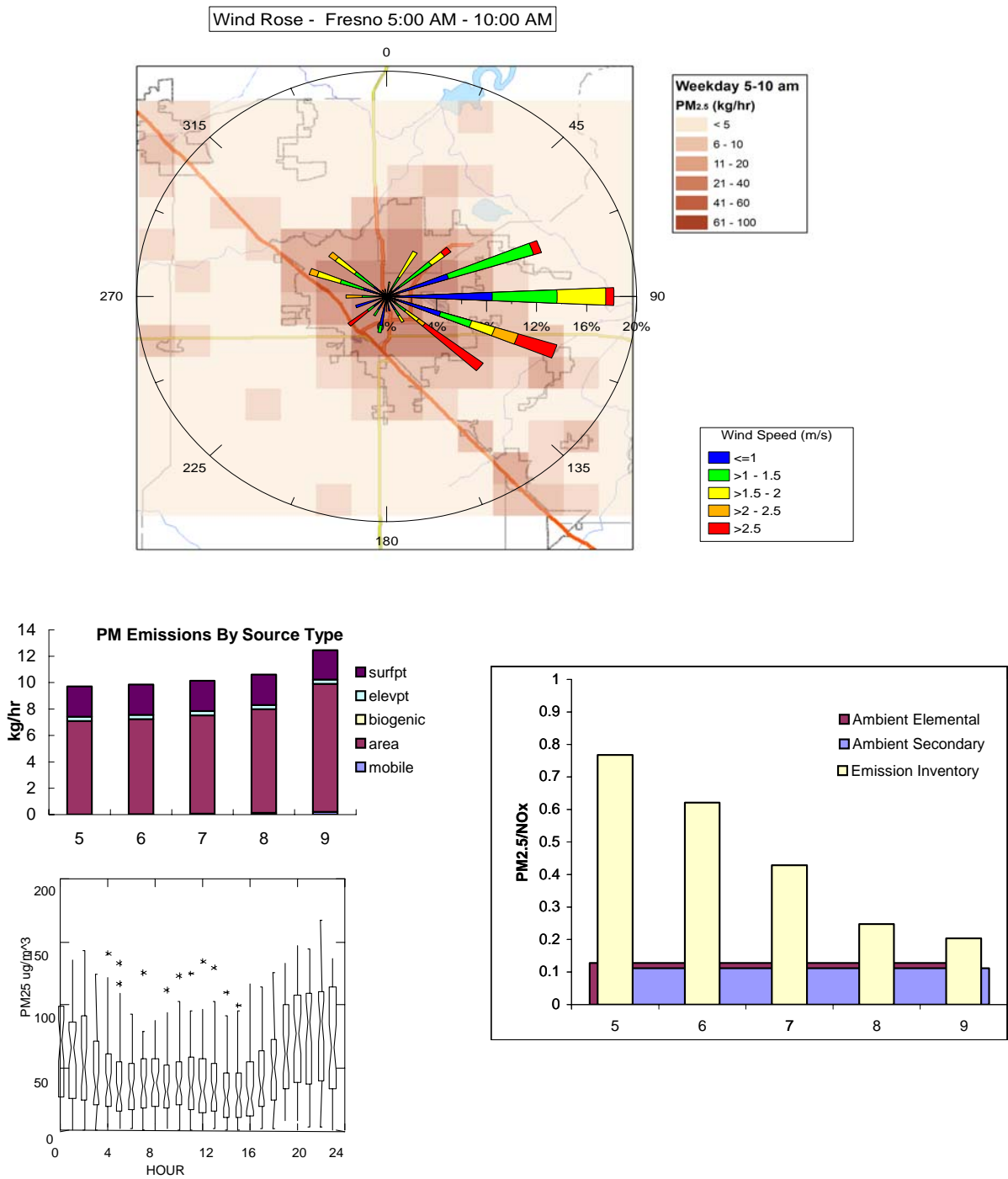
Figure 3-21. Fresno First Street PM$_{2.5}$/NO$_x$ summary sheet.

4. FINDINGS AND RECOMMENDATIONS

4.1 SUMMARY FINDINGS

The following findings resulted from this task:

- Assuming NO_x emissions are reasonably certain, VOC emissions estimates are within 50% at Fresno First Street. Comparability is best in the early morning hours (usually 0700 PST or earlier).

- CO/NO_x ratios from the emission inventory are consistently lower than those from ambient data. This discrepancy suggests that CO emissions are underestimated. The largest discrepancy occurs at sites dominated by area sources, particularly on the weekends.

- Bakersfield data showed good agreement among emission inventory and ambient SO_2/NO_x ratios in the late morning hours (usually 0800 PST or later), particularly when elevated point sources were excluded from the analysis. The emission inventory does not capture the reduced SO_2/NO_x ratio that occurs in the ambient data on weekend days.

- The Bethel Island site violates a basic assumption of ratio reconciliation analysis, that of fresh emissions dominating morning concentrations. Therefore, results from Bethel Island are of limited value.

- $PM_{2.5}$ estimates from area sources, which dominated the PM emission inventory, may be overestimated. All $PM_{2.5}/NO_x$ ratios calculated from emission inventory data were higher than those calculated from ambient data. This analysis requires several assumptions that increase the uncertainty of the results relative to the other pollutants. Fresno was the only site analyzed that showed an increase in measured $PM_{2.5}$ concentrations in the morning hours (see Figure 3-20).

- Improvements to the area source emission estimates would most benefit the emission inventory overall. Ratios for sites and pollutants dominated by area sources did not compare as well as sites or pollutants dominated by mobile or point sources. The sudden increase in NO_x emissions from area sources, which occurs between 0700 and 0800 PST, appears especially suspect. This pattern is most pronounced in Bakersfield. Therefore, an investigation of the temporal patterns of NO_x emissions from area sources and the spatial patterns that concentrate area-source NO_x in the Bakersfield area is recommended.

- With the exception of VOCs, emission inventory ratios are most comparable for the late morning hours (usually 0800 PST or later). The VOC/NO_x ratios show the opposite trend.

4.2 COMPARISON TO PREVIOUS EVALUATIONS

An emission inventory reconciliation in the SJV was performed as part of the Integrated Monitoring Study 1995 (IMS-95). This section highlights the improvements made since that study, as well as aspects of the emission inventory that still could be improved.

- Comparisons of weekday versus weekend inventory emissions for CO and NO_x in IMS-95 showed little variation in daily emission rates and diurnal profiles. These comparisons have been improved, particularly with respect to mobile sources. However, the emission inventory still does not fully take into account variations in weekday and weekend emissions for area source activities.

- PM_{10}/NO_x ratios were analyzed in IMS-95, and the emission inventory ratios were found to be two to three times higher than ambient ratios for Bakersfield and Fresno. We found similar discrepancies for $PM_{2.5}/NO_x$ ratios. PM may still be overestimated in the emission inventory.

- IMS-95 results suggested that mobile source emissions were estimated better than area or point source emissions. Point source inventories may have improved, as evidenced by good SO_2/NO_x ratio comparisons at Bakersfield; however, area source emission estimates still need improvement.

- Ambient ratios of non-methane hydrocarbons (NMHC) to NO_x were about two times higher than emission inventory ratios at Fresno in IMS-95, suggesting that mobile source VOC emissions may have been underestimated in Fresno. This study found an ambient VOC/NO_x ratio only 1.5 times higher than the emission inventory ratio. Mobile source emissions in Fresno appear to be better estimated than previously.

- In IMS-95, a rural site with limited emissions (Kern Wildlife Refuge) was studied and found to be unsuited for performing ratio comparisons. We experienced similar issues at Bethel Island.

4.3 RECOMMENDATIONS

To improve the emission inventory, we recommend that ARB consider the following:

- Investigate the primary sources of species (such as CO and $PM_{2.5}$) and the sites (especially Bakersfield) showing the greatest discrepancies from a bottom-up perspective (e.g., assess the representativeness of emission factors and activity data used to prepare the emission inventory).

- Review, and change as needed, the temporal and spatial allocation factors and speciation profiles used to prepare the hourly, gridded, speciated emission inventory so that ratios better match ambient temporal trends (such as hourly and weekday-weekend differences).

- Investigate area source emissions in particular. These sources represent a large portion of the emission inventory and improving these emissions estimates would substantially impact subsequent analyses.

5. REFERENCES

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Haste T.L., Chinkin L.R., Kumar N., Lurmann F.W., and Hurwitt S.B. (1998) Use of ambient data collected during IMS95 to evaluate a regional emission inventory for the San Joaquin Valley. Final report prepared for the San Joaquin Valleywide Air Pollution Study Agency, c/o the California Air Resources Board, Sacramento, CA, by Sonoma Technology, Inc., Petaluma, CA, STI-997211-1800-FR, July.

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Omar A., Winker D., and Won J. (2004) Aerosol models for the CALIPSO lidar inversion algorithms. In proceedings of *SPIE - Laser Radar Technology for Remote Sensing*, 5240, 153-164, C. Werner, ed. (10.1117/12.511067). Available on the Internet at http://spiedl.aip.org/getabs/servlet/GetabsServlet?prog=normal&id=PSISDG005240000001000153000001&idtype=cvips&gifs=Yes&bproc=volrange&scode=5200%20-%205299.

APPENDIX A

CHEMICAL SPECIES CROSS-REFERENCE LIST

Group Number	Group Name	Ambient Species in Group	EI Species in Group
1	Ethane	Ethane	ethane
2	Ethylene	Ethylene	ethylene
3	Acetylene	Acetylene	acetylene
4	Propane	Propane	propane
5	Propene	Propene	propylene
6	i-Butane	i-Butane	isobutane
7	i-Butene	i-Butene	isobutylene
8	1-Butene	1-Butene	1-butene
9	1,3-Butadiene	1,3-Butadiene	1,3-butadiene
10	n-Butane	n-Butane	n-butane
11	trans-2-Butene	trans-2-Butene	trans-2-butene
12	2,2-Dimethylpropane	2,2-Dimethylpropane	2,2-dimethylpropane
13	cis-2-Butene	cis-2-Butene	cis-2-butene
14	3-Methyl-1-butene	3-Methyl-1-butene	3-methyl-1-butene
15	i-Pentane	i-Pentane	isopentane
16	1-Pentene	1-Pentene	1-pentene
17	2-Methyl-1-butene	2-Methyl-1-butene	2-methyl-1-butene
18	n-pentane	n-pentane	n-pentane
19	Isoprene	Isoprene	isoprene
20	trans-2-Pentene	trans-2-Pentene	trans-2-pentene
21	cis-2-Pentene	cis-2-Pentene	cis-2-pentene
22	2-Methyl-2-butene	2-Methyl-2-butene	2-methyl-2-butene
23	2,2-Dimethylbutane	2,2-Dimethylbutane	2,2-dimethylbutane
24	Cyclopentene	Cyclopentene	cyclopentene
25	4-Methyl-1-pentene	4-Methyl-1-pentene	4-methyl-1-pentene
26	Cyclopentane	Cyclopentane	cyclopentane
27	2,3-Dimethylbutane	2,3-Dimethylbutane	2,3-dimethylbutane
28	cis-4-Methyl-2-pentene	cis-4-Methyl-2-pentene	4-methyl-cis-2-pentene
29	2-Methylpentane	2-Methylpentane	2-methylpentane
30	3-Methylpentane	3-Methylpentane	3-methylpentane
31	2-Methyl-1-pentene	2-Methyl-1-pentene	2-methyl-1-pentene
32	1-Hexene	1-Hexene	1-hexene
33	n-Hexane	n-Hexane	n-hexane
34	trans-2-Hexene	trans-2-Hexene	trans-2-hexene
35	2-Methyl-2-pentene	2-Methyl-2-pentene	2-methyl-2-pentene
36	cis-2-Hexene	cis-2-Hexene	cis-2-hexene
37	Methylcyclopentane	Methylcyclopentane	methylcyclopentane
38	2,4-Dimethylpentane	2,4-Dimethylpentane	2,4-dimethylpentane
39	MTBE	MTBE	methyl t-butyl ether (mtbe)
40	Benzene	Benzene	benzene
41	Cyclohexane	Cyclohexane	cyclohexane
42	2-Methylhexane	2-Methylhexane	2-methylhexane
43	2,3-Dimethylpentane	2,3-Dimethylpentane	2,3-dimethylpentane
44	3-Methylhexane	3-Methylhexane	3-methylhexane

Group Number	Group Name	Ambient Species in Group	EI Species in Group
45	2,2,4-Trimethylpentane	2,2,4-Trimethylpentane	2,2,4-trimethylpentane
46	n-Heptane	n-Heptane	n-heptane
48	Methylcyclohexane	Methylcyclohexane	methylcyclohexane
49	2,4,4-Trimethyl-2-pentene	2,4,4-Trimethyl-2-pentene	2,4,4-trimethyl-2-pentene
50	2,5-Dimethylhexane	2,5-Dimethylhexane	2,5-dimethylhexane
51	2,4-Dimethylhexane	2,4-Dimethylhexane	2,4-dimethylhexane
52	2,3,4-Trimethylpentane	2,3,4-Trimethylpentane	2,3,4-trimethylpentane
53	Toluene	Toluene	toluene
54	2,3-Dimethylhexane	2,3-Dimethylhexane	2,3-dimethylhexane
55	2-Methylheptane	2-Methylheptane	2-methylheptane
56	3-Ethylhexane	3-Ethylhexane	3-ethylhexane
57	2,2-Dimethylheptane	2,2-Dimethylheptane	2,2-dimethylheptane
58	2,2,4-Trimethylhexane	2,2,4-Trimethylhexane	2,4,4-trimethylhexane
59	n-Octane	n-Octane	n-octane
60	Ethylcyclohexane	Ethylcyclohexane	ethylcyclohexane
61	Ethylbenzene	Ethylbenzene	ethylbenzene
62	m-Xylene & p-Xylene	m-Xylene & p-Xylene	m-xylene
			p-xylene
63	Styrene	Styrene	styrene
64	o-Xylene	o-Xylene	o-xylene
65	n-Nonane	n-Nonane	n-nonane
66	i-Propylbenzene	i-Propylbenzene	isopropylbenzene (cumene)
67	n-Propylbenzene	n-Propylbenzene	n-propylbenzene
68	p-Ethyltoluene	p-Ethyltoluene	1-methyl-4-ethylbenzene
69	m-Ethyltoluene	m-Ethyltoluene	1-methyl-3-ethylbenzene
71	o-Ethyltoluene	o-Ethyltoluene	1-methyl-2-ethylbenzene
73	n-Decane	n-Decane	n-decane
74	alpha-Pinene	alpha-Pinene	a-pinene
75	beta-Pinene	beta-Pinene	b-pinene
76	delta 3-Carene	delta 3-Carene	3-carene
77	d-Limonene	d-Limonene	d-limonene {4-isopropenyl-1-methylcycohexane}
79	Ethanol	Ethanol	ethanol
80	Acetone	Acetone	acetone
81	2-Butanone	2-Butanone	methyl ethyl ketone (mek) (2-butanone)
82	(Acetic Acid)	(Acetic Acid)	acetic acid
83	Pentanal	Pentanal	c5 aldehyde
84	Hexanal	Hexanal	hexaldehyde
86	Benzaldehyde	Benzaldehyde	benzaldehyde
108	Trimethylbenzenes	1,2,3-Trimethylbenzene 1,2,4-Trimethylbenzene & sec-Butylbenzene 1,3,5-Trimethylbenzene	1,2,4-trimethylbenzene 1,3,5-trimethylbenzene (1-methylpropyl)benzene trimethylbenzene 1,2,3-trimethylbenzene

Group Number	Group Name	Ambient Species in Group	EI Species in Group
109	Unidentified Hydrocarbons	Unidentified Hydrocarbons	
			cyclohexene
			2,3,3-trimethylpentane
			4-methyl-trans-2-pentene
			4-methylheptane
			3-methylheptane
			3-ethylpentane
			1,2,4-trimethylcyclopentene
			1,3-diethylbenzene (meta)
			1,4-diethylbenzene (para)
			t-butylbenzene
			2,2,4-trimethylhexane
			(2-methylpropyl)benzene
			1,4-dimethyl-2-ethylbenzene
			1,3-dimethyl-4-ethylbenzene
			1,2-dimethyl-4-ethylbenzene
			1,3-dimethyl-2-ethylbenzene
			1,2-dimethyl-3-ethylbenzene
			1,3-dimethyl-5-ethylbenzene
			2-methyl-2-hexene
			3-methyl-cis-2-hexene
			3,3-dimethylpentane
			2-methylnonane
			2,4-dimethyl-2-pentene
			cis-1-methyl-3-ethylcyclopentane
			ethylmethylcyclohexanes
			trans-1,3-pentadiene
			butylcyclohexane
			propylcyclohexane
			isopropylcyclohexane
			2-methyl-trans-3-hexene
			cis-1,3-dimethylcyclopentane
			trans-1,3-dimethylcyclopentane
			trans-1-2-dimethylcyclopentane
			trans-2-heptene
			cis-2-heptene
			1,1,3-trimethylcyclopentane
			1,1,2-trimethylcyclopentane
			2-methyl-3-ethylpentane
			cis-1,trans-2,3-trimethylcyclopentane
			1,1-dimethylcyclohexane
			trans-1-methyl-3-ethylcyclopentane

Group Number	Group Name	Ambient Species in Group	EI Species in Group
			1,1-methylethylcyclopentane
			cis-1,4-dimethylcyclohexane
			cis-1,2-dimethylcyclohexane
			1,1,4-trimethylcyclohexane
			4,4-dimethylheptane
			cis-1,cis-3,5-trimethylcyclohexane
			3,3-dimethylheptane
			1,1,3-trimethylcyclohexane
			3,4-dimethylheptane
			3-ethylheptane
			3,6-dimethyloctane
			3-ethyloctane
			3-methylnonane
			trans-1,methyl-2n-propylcyclohexane
			1-methyl-2-isopropylbenzene
			1,2,4,5-tetramethylbenzene
			1,2,3,5-tetramethylbenzene
			5-methylindan
			4-methylindan
			2-methylindan
			1,2,3,4-tetramethylbenzene
			1-methyl-4-ethylcyclohexane
			1-heptene
			trans-3-heptene
			2,2,5-trimethylhexane
			indan
			naphthalene
			ethylcyclopentane
			trans-1,3-dimethylcyclohexane
			trimethylcyclohexane
			1,3,5-trimethylcyclohexane
			diethylcyclohexane
			dimethylheptanes
			trans-3-hexene
			2,2-dimethylhexane
			2,3,5-trimethylhexane
			2,4-dimethylheptane
			2,5-dimethylheptane
			3,5-dimethylheptane
			2,3-dimethylheptane
			2-methyloctane
			2,4,5-trimethylheptane
			2,4-dimethyloctane
			3,4-dimethylhexane

Group Number	Group Name	Ambient Species in Group	EI Species in Group
			3,4-dimethyloctane
			1-methyl-3n-propylbenzene
			1-methyl-3-isopropylbenzene
			1,2-diethylbenzene (ortho)
			2,6-dimethylheptane
			3,3-dimethyl-1-butene
			3-methyloctane
			4-methyloctane
			2,2,4-trimethylheptane
			2,2-dimethyloctane
			2,5-dimethyloctane
			2,6-dimethyloctane
			1-methyl-2n-propylbenzene
			cis-1,3-dimethylcyclohexane
			trans-1,4-dimethylcyclohexane
			1-methyl-4n-propylbenzene
			2,3-dimethyloctane
			3,3-dimethyloctane
			1-methyl-3-isopropylcyclohexane
			1-methyl-2-isopropylcyclohexane
			1,1,3,4-tetramethylcyclohexane
			1,2-dimethyl-3-ethylcyclohexane
			1-ethyl-3-methylcyclopentane
			cis,cis-1,2,4-trimethylcyclohexane
			2-ethyl-1,3-dimethylcyclohexane
			1,2,4-trimethylcyclopentane
			1,2,3-trimethylcyclopentane
			trans,cis-1,2,4-trimethylcyclohexane
			trans,trans-1,3,5-trimethylcyclohexane
			1,2,3-trimethylcyclohexane
			cis,trans-1,2,4-trimethylcyclohexane
			trans-1-ethyl-3-methylcyclohexane
			trans-1-ethyl-4-methylcyclohexane
			1-ethyl-2-methylcyclopentane
			pentylcyclopentane
			1-methylindan
			1,2,4-trimethylcyclohexane
			isobutylcyclohexane

Group Number	Group Name	Ambient Species in Group	EI Species in Group
			1,2-dimethylcyclopentane
			cis-bicyclo[4.3.0]nonane
			trans-1-ethyl-2-methylcyclohexane
			3-ethyl-2-methylheptane
			3,5-dimethyloctane
			4,5-dimethyloctane
			4-methylnonane
			cis-1-ethyl-3-methylcyclohexane
110	Not in EI	Octanal	
		Nonanal	
		Decanal	
		2,4,4-Trimethyl-1-pentene	
		Heptanal	
		2-Octanone	

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